# **PREFACE**

"Inorganic Chemistry for Competitions" has primarily, been written with the aim of meeting the needs and interests of students seeking admission to professional courses especially in engineering and medical. This is an age of tough competition where only the best survives. No doubt, the syllabus for various entrance tests is nearly the same as for intermediate or 10+2 examinations, yet even good students fail to qualify as the standard of these tests is comparatively high and seats in engineering and medical colleges are limited.

The present trend in competitive examinations is the stress on an objective rather than subjective treatment of the subject matter. A critical scrutiny of the question papers of previous years of various entrance tests reveals that a variety of questions such as very short answer type, short answer type, fill in the blanks, true and false, match the column, multiple choice, numerical type are usually asked. In order to answer these questions, the students must be well equipped with thorough knowledge of the subject and its application. With these objectives in mind, I have tried to present inorganic chemistry for competitions covering whole of the syllabus of nearly all the competitions. The complete subject matter has been arranged in a systematic manner. Every topic has been dealt precisely and to the point in a simple and understandable language. Things have been explained with proper reasoning wherever possible. A good number of illustrations and solved problems based on structure and properties including numerical problems have been provided to understand the theoretical aspect. Due emphasis has been given on group discussions of various groups of periodic table. Flow-sheet diagrams have been provided to simplify the extraction of various metals, preparation of a number of compounds and their properties. At the end of each chapter, a good number of questions of various types have been given for self-assessment. It is my belief that students will be duly rewarded if they attempt these questions honestly and sincerely after learning the particular topic. Necessary hints have been given wherever it is felt necessary.

Human efforts are never perfect. In spite of my best efforts, I am aware of the possible errors and omissions that have escaped my notice. I shall, therefore, be extremely thankful to the learned teachers who will extend their cooperation by sending their valuable criticism, suggestions and observations for further improvement of the book. I consider it my duty to pay thanks to the authors and publishers of the books which I have consulted during the preparation of the manuscript.

My sincere thanks are due to Shri Manoj Kumar Bathla, Proprietor, M/s G.R. Bathla & Sons, Shri Shiv Charan Sohal (Artist) for the whole-hearted cooperation in the preparation and publication of this book. I am also thankful to Dr. A.K. Virmani and Dr. A.S. Singh for their encouragement, cooperation and guidance in the preparation of the manuscript of this book. Finally, I thank my wife and children for the help they have extended in proof-reading.

June, 2000 O.P. TANDON



Chapters Page No.

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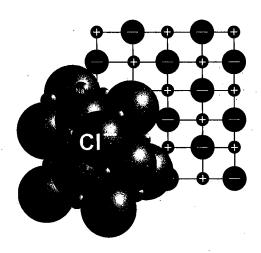
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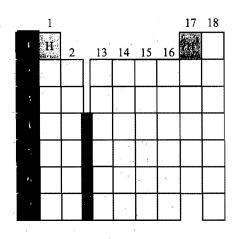
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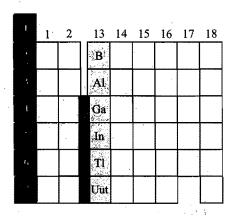
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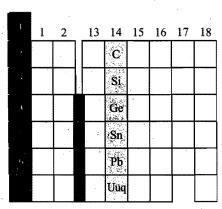
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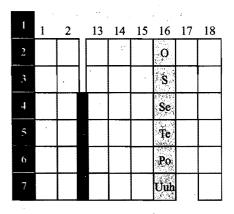
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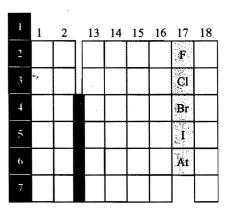
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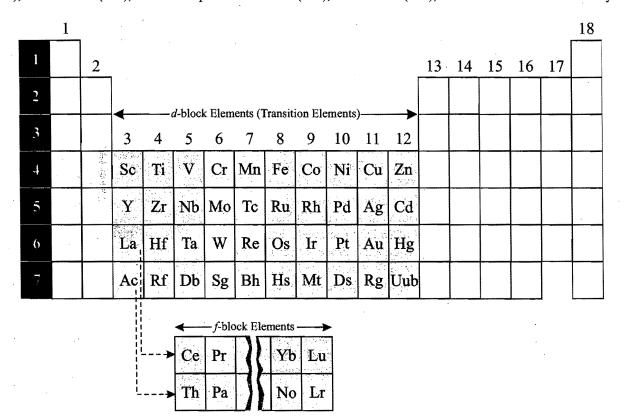
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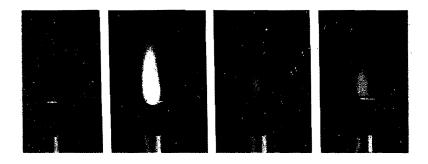
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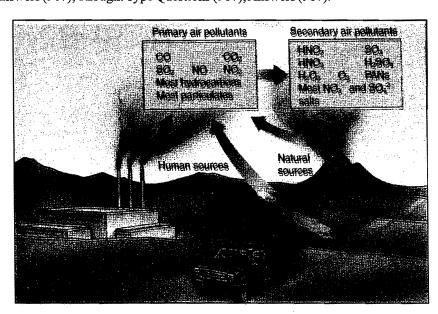
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### **Environmental Chemistry**

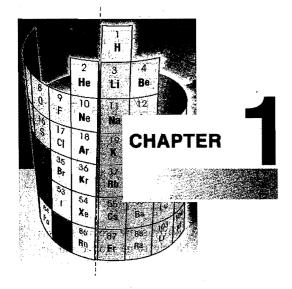
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# Classification of Elements and Periodicity in Properties

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- 1.3 Mendeleev's Periodic Law and Original Periodic Table
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# 1.1 INTRODUCTION

### Object and Need of Classification of Elements

Elements are the basic constituents of all types of matter. The discovery of chemical elements has been an ongoing process since ancient times. Certain elements, such as gold, appear in nature in elemental form and were thus discovered thousands of years ago. In contrast, some elements are radioactive and intrinsically unstable. The majority of the elements although stable are dispersed widely in nature and incorporated into numerous compounds. For centuries, therefore, scientists were unaware of their existence. At the beginning of the eighteenth century, only a few elements were known. During eighteenth and early nineteenth century, advances in chemistry made it easier to isolate elements from their compounds. As a result, the number of known elements had more than doubled from 31 in 1800 to 63 by 1865. At present, 117 elements\* are known. Out of these, recently discovered elements are not natural but synthetic, *i.e.*, man-made and efforts are still going on to synthesise new elements by artificial transmutation.

As the number of known elements increased, it became rather impossible to study individually the chemistry of these elements and their innumerable compounds and scientists began to investigate the possibilities of classifying them in useful ways. The basic object and need of classification can be best stated in the words of Huxley, "The actual or ideal arrangement together of those which are alike and separation of those which are unlike; the purpose of this arrangement being primarily to disclose the correlations, or laws of union, or properties, or circumstances and secondarily to facilitate the operation

<sup>\*</sup>Recently, elements with atomic numbers 113, 114, 115, 116 and 118 have been reported.

of the mind in clearly receiving and then retaining in the memory the characteristics of the objects in question." In short, it can be stated that the basic object of classification is to arrange the facts regarding elements and their compounds in such a way so that we may have greatest control over their characteristics with least possible effort. The best classification would be one which puts together those elements which resemble in most respects and separates other.

Attempts were made to classify the elements according to one property or the other. The elements were classified into metals and nonmetals; into electropositive and electronegative. They were classed according to their valency as monovalent, divalent, trivalent, etc. In these classifications, the same element frequently appeared in more than one class and hence all these early classifications were considered as rough classifications. After the establishment of Dalton's atomic theory, the chemists took atomic mass as the fundamental property of the element and tried to seek a relationship between the properties of the elements and their atomic masses. A number of classifications, taking atomic masses of the elements as the basis, were presented. The best formulation resulted in the form of periodic table in which elements have been arranged according to their properties in a tabular form. The elements belonging to same vertical column constitute a chemical family having similar properties.

The arrangement of elements in order of increasing atomic masses, with elements having similar properties in vertical columns, is known as periodic table. The periodic classification (long or extended form of periodic table) of elements has extremely simplified the study of such a large number of elements.

# 1.2 EARLIER ATTEMPTS OF CLASSIFICATION OF ELEMENTS (Brief Historical Development of the Periodic Table)

Some of the earlier classifications based on atomic masses of the elements are described below:

#### 1. Döbereiner's Law of Triads

Döbereiner between 1815 and 1829 gave his law of triads. According to which in certain triads (groups of three elements which possessed similar chemical properties) the atomic mass of the central element was merely the arithmetic mean of the atomic masses of the other two elements and the properties of the middle element were in between those of the end members. These families of three elements became known as Döbereiner's Triads. But in some triads, all the three elements possessed nearly the same atomic masses, hence the law was rejected.

#### DÖBEREINER'S TRIADS

7	Triads		Mean of atomic masses of 1st and 3rd elements
Li	Na	K	$\frac{7+39}{2} = 23$
7	23	39	2 - 20
Cl	Br	I	35.5 + 127 - 81.25
35.5	80	127	$\frac{81.25}{2} = 81.25$
Ca	Sr	Ba	$\frac{40 + 137}{2} = 88.5$
40	. 88	137	2 = 88.5
S	Se	Te	32 + 127
32	79	127	$\frac{32}{2} = 79.5$
P	$\mathbf{A}\mathbf{s}$	Sb	$\frac{31+120}{2}=75.5$
31	75	120	<del>2</del> = 75.5
Fe	Co	Ni	Nearly same atomic masses
Ru	Rh	Pd	Nearly same atomic masses
Os	Ir	Pt	Nearly same atomic masses

The main drawback of this classification was that the concept was not applicable to all the known elements but only to a limited number of elements. However, one point became clear that properties of the elements have some relationship with their atomic masses.

# 2. De-Chancourtois Classification (The Telluric Helix)

In 1862, A.E. de Chancourtois a French geologist, made the next attempt to classify the elements on the basis of their atomic masses. He took a vertical cylinder with 16 equidistant lines on the surface of the cylinder. The lines were parallel to the axis of the cylinder. A helix at 45° to the axis was drawn and the elements in the increasing order of their atomic masses were arranged on the helix. He observed that elements which differed from each other in atomic mass 16 or multiples of 16 fell in a vertical line from the centre of the spiral. The elements in a vertical line showed nearly the same properties. However, this classification was not accepted.

#### 3. Newland's Law of Octaves

The first attempt to classify all the known elements was made by Newland in 1864. He presented the law of octaves. According to this law, the elements when arranged in order of their increasing atomic masses, the eighth succeeding element was the repetition of the first one like 8th note of the musical scale, i.e., after a difference of seven, elements with similar characteristics were observed. The following are the three horizontal rows of the Newland's classification:

Musical	scale:	Sa.	Re	Ga	Ma	- Pa	Dha	- Ne
		1	.2	3	4	5	6	7
	1st	H	Li	Be	В	$\mathbf{C}_{\perp}$	N.	. 0
*	2nd	F	Na	Mg	Al	Si .	P	S
	3rd	Cl	K	Ca	Cr	Ti	Mn	Fe

The system worked quite well for the lighter elements. For example, H, F and Cl show similar properties and similarly

Li, Na and K exhibit same characteristics. The system, however, fails in the case of heavier elements as manganese has been placed along with nitrogen and phosphorus or iron has been placed along with oxygen and sulphur, i.e., dissimilar elements have been grouped which is against the aim of classification. This clearly shows that in the classification, the properties of the elements were not taken into account and only the elements were arranged in order of ascending atomic masses. No space was left for the elements which were unknown at that time and many elements were provided wrong positions on account of wrong values of atomic masses in this classification. Thus, Newland's classification was not accepted as an appropriate arrangement. However, his work was recognised by Royal Chemical Society, London, and was awarded Davy Medal in 1887.

### 4. Lother Meyer's Curve

Lother Meyer in Germany and Mendeleev in Russia quite independently evolved, in 1869, identical classifications of elements. Both these classifications emphasised the periodicity of the properties of the elements with their atomic masses. While Mendeleev's classification was based largely on considerations of chemical properties of the elements, that of Lother Meyer emphasised physical characteristics of the elements. Lother Meyer presented the classification in the form of curve while Mendeleev in the form of a table.

Lother Meyer calculated the atomic volumes of the known elements by applying formula,

Atomic volume = 
$$\frac{\text{Atomic mass}}{\text{Density}}$$

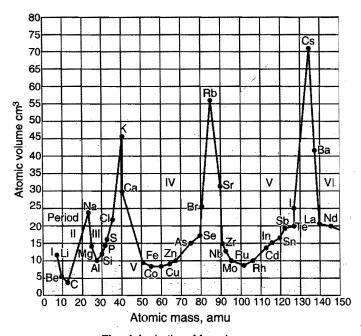


Fig. 1.1 Lother Meyer's curve

When he plotted these atomic volumes against corresponding atomic masses, a curve taking the form of sharp peaks and broad minima was obtained (Fig. 1.1).

Lother Meyer pointed out that elements having similar properties occupy similar positions on the curve such as,

- (i) Alkali metals, having the largest atomic volumes, occupy the maxima of the curve.
- (ii) The alkaline earth metals (Mg, Ca, Sr, Ba) occupy positions at about the mid-points on the descending portions of the curve.
- (iii) The halogens (F, Cl, Br, I) occupy positions on the ascending portions of the curve.
- (iv) The transition elements occupy minima of the curve. On the basis of above observations Lother Meyer proposed that, the physical properties of the elements are a periodic function of their atomic masses.

[Later on when atomic numbers of the elements were plotted in place of atomic masses, the general pattern of the curve remained the same.]

It was an ideal classification but lacked in practical utility as it was not easy to keep in mind the various portions of the curve.

# 1.3 MENDELEEV'S PERIODIC LAW AND ORIGINAL PERIODIC TABLE

Mendeleev put forward the periodic law which forms the basis of modern classification of elements in the form of a table, known as the periodic table. The periodic law can be stated as, "If the elements are arranged in order of increasing atomic masses, their properties vary in definite manner from member to member of the series, but return more or less nearly to same value at certain fixed points in the series". In other words the properties of the elements are a periodic function of their atomic masses. This was an impressive version of law of octaves. The main points of periodic law as stated by Mendeleev in his original paper are reproduced below:

- 1. The elements, if arranged according to their atomic weights exhibit an evident periodicity of properties.
- **2.** Elements which are similar as regards their chemical properties have atomic weights which either are of nearly same value, *e.g.*, Fe, Co, Ni or increase regularly, *e.g.*, K, Rb, Cs.
- 3. The arrangement of elements or groups of elements in the order of their atomic weights corresponds to their so called "valencies" as well as their distinctive properties.
- 4. The elements which are most widely distributed in nature have small atomic weights and possess sharply defined properties.
- 5. The magnitude of atomic weight determines the character of the element.
  - 6. Many yet unknown elements may be discovered.
- 7. The atomic weight of an element may sometimes be corrected with the aid of the knowledge of the atomic weights of the adjacent elements.

**8.** Certain characteristic properties of elements can be foretold from their atomic weights.

Mendeleev's original table prepared in the light of the above statements arranged similar elements in horizontal rows but subsequently he modified the original table arranging similar elements in vertical columns. The original modified periodic table, is shown in Fig. 1.2.

A tabular arrangement of elements in rows and columns, highlighting the regular repetition of properties of elements is called a periodic table.

Mendeleev arranged the elements between hydrogen and uranium, providing 90 spaces between these two elements, in order of increasing atomic masses. Elements with similar properties were present in vertical columns called **groups**. The horizontal rows were called **periods**. Mendeleev violated his periodic law at certain places to give appropriate position to the few elements on the basis of their

properties, *i.e.*, he laid emphasis on the properties of the elements rather than their atomic masses. For example, iodine having lower atomic mass than tellurium was placed ahead of tellurium because iodine showed similarities with fluorine, chlorine and bromine.

When Mendeleev presented the periodic table, only 63 elements were known. Thus, a number of gaps for unknown elements were left in the table and the properties of these unknown elements were predicted on the basis of periodic law. These predicted properties helped the future scientists in the discovery of unknown elements. For example, gallium and germanium were not known when Mendeleev presented the periodic table. These elements were named eka-aluminium and eka-silicon. Their properties were predicted by Mendeleev and these properties actually matched the properties of elements when discovered.

Mendeleev's	Original	Periodic	Table of	Elements
-------------	----------	----------	----------	----------

Series	Gṛoup I R₂O	Group II RO	Group III R <sub>2</sub> O <sub>3</sub>	Group IV RO <sub>2</sub> /RH <sub>4</sub>	Group V RH <sub>3</sub> /R <sub>2</sub> O <sub>5</sub>	Group VI RH <sub>2</sub> /RO <sub>3</sub>	Group VII RH/R <sub>2</sub> O <sub>7</sub>	Group VIII RO <sub>4</sub>
1.	H = 1			·				
2.	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3.	Na = 23	Mg = 24	A1 = 27.3	Si = 28	P = 31	S = 32	C1 = 35.5	
4.	K = 39	Ca = 40	= 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59 Ni = 59, Cu = 63
5.	(Cu = 63)	Zn = 65	= 68	= 72	As = 75	Se = 78	Br = 80	
6.	Rb = 85	Sr = 87	*Yt = 88	Zr = 90	Nb = 94	Mo = 96	= 100	Ru = 104, Rh = 10 Pd = 106, Ag = 10
7.	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 128	I = 127	
8.	. Cs = 133	Ba = 137	*Di = 138	*Ce = 140				
9.							_	
10.			*Er = 178	*La = 180	Ta = 182	W = 184		Os = 195, Ir = 19 Pt = 198
11.	(Au = 199)	Hg = 200	T1 = 204	Pb = 207	Bi = 208			
12.	-			Th = 231		U = 240		

Fig. 1.2 Mendeleev's Periodic Table (Published in 1872)

The table given below gives a comparative idea about the predicted and actually observed some of the properties of these elements.

Property	Eka-aluminium (Predicted)			Germanium (Observed)
Atomic mass	68	70	72	72.6
Density (g/cm <sup>3</sup> )	5.9	5.94	5.5	5.36
Formula of oxide	E <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>	EO <sub>2</sub>	GeO <sub>2</sub>
Formula of chloride	ECl <sub>3</sub>	GaCl <sub>3</sub>	ECl <sub>4</sub>	GeCl <sub>4</sub>

Atomic weight is now referred as atomic mass.

The original periodic table consisted eight vertical columns called **groups** (Fig. 1.2). Each group consisted elements having similar properties, especially the same valency. This table consisted a number of defects such as anomalous pairs, position of isotopes, position of lanthanides and actinides, etc. Some of these defects do not exist in modern Mendeleev periodic table.

# 1.4 MODERN PERIODIC LAW AND MODIFIED FORM OF MENDELEEV'S PERIODIC TABLE

As the physical and chemical properties of an element depend on the number of electrons and their arrangement in various energy shells of the atom, the atomic number (the number of positive charges on the nucleus or number of electrons in energy shells) is thus the fundamental property of the element. The change in atomic number always changes the fate of the element, *i.e.*, a new element comes into existence. **Moseley**, thus, suggested that basis of classification of elements should be the **atomic numbers** of the elements rather than the **atomic masses** of the elements. He

modified the periodic law by saying that physical and chemical properties of the elements are periodic function of their atomic numbers. When the elements are arranged in order of their increasing atomic numbers, the same table as presented by Mendeleev, is obtained. The table based on atomic numbers of the elements is called modern Mendeleev's periodic table (Fig. 1.3). In modern periodic table, similar properties recur after the intervals of 2, 8, 8, 18,

#### Modern (Modified) Mendeleev's Periodic Table

GROUP	I		I	I		III		IV		v	VI			VII .	,	VIII		0
PERIOD	Α	В	Α	В	Α	В	A	В	Α	В	Α	В	Α	В				
1	Н												Н					He
*	1												1					2
2	Li		Ве		В		C		N		0		F					Ne
	3		4		5		6		7		8		9 .					10
3	Na		Mg		Al		Si		P		s	ļ	Cl					Ar
	11		12		13		14		15		16		17					18
	K		Ca			Sc		Ti	٠.	V		Cr		Mn	Fe	Co	Ni	
	19		20			21		22		23		24		25	26	27	28	Kr
4		Cu		Zn	Ga		Ge		As		Se		Br					36
		29		30	31		32		33		34		35					
	Rb		Sr			Y		Zr		Nb		Mo		Тс	Ru	Rh	Pd	
	37		38		_	39		40	,	41		42	_	43	44	45	46	Xe
2 P 5		Ag		Cd	In		Sn		Sb		Te		I					54
		47		48	49	· · · · · · · · · · · · · · · · · · ·	50		51		52		53		·			
,	Cs		Ba			La*		Hf		Ta		W		Re	Os	Ir	Pt	_
	55		56	¥ T .	77	57-71	Tu.	72	n:	73		74		75	76	77	78	Rn
		Au 79		Hg 80	T1 81		Pb 82	•	Bi 83		Po 84		At 85			4		86
	-		_		61	. +	02	T/ /DO	83			~ `	0.5	T.T. (701.)			* *	
	Fr 87		Ra 88			Ac <sup>†</sup> 89-103		Ku(Rf) 104		Ha	Unh(	Sg) 106		Uns(Bh) 107	Uno	Une	Uun	
7	8/.	Uuu	1	Uub	Uut		Uuq.	104	Uup	105	Uuh	100		107	(Hs) 108	(Mt) 109	110	Uuo
1		111		112	113		114		115		116			_	100	10)	110	118
		111		112	113		11.7		113		110							110

← − − − − − − − Inner Transition Elements − − − − − − →

*Lanthanide	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Уb	Lu
series	58	59	.60	61	62	63	64	65	66	67	68	69	70	71
<sup>†</sup> Actinide	<b>Th</b>	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
series	90	91	92	93	94	95	96	97	98	99	100	101	102	103

Fig. 1.3 Modern Mendeleev's Periodic Table

18 and 32 elements, *i.e.*, if the elements are arranged in the increasing atomic numbers, the properties of the elements reappear after definite regular intervals. With the replacement of atomic mass by atomic number as the basis of classification, two main defects of original table based on atomic masses disappear. These defects are:

(i) Anomalous pairs: The original periodic law based on atomic masses is violated in case of four pairs of elements in order to give them positions on the basis of properties. The elements having higher atomic masses have been assigned positions before the elements having lower atomic masses at four places as shown below:

This defect disappears, if the elements are arranged in order of increasing atomic numbers.

(ii) Position of isotopes: Isotopes are atoms of the same element having different atomic masses but same atomic number. The isotopes of the same element will be given different positions, if atomic mass is taken as a basis. This shall disturb the symmetry of the table. In modern table, one position is fixed for one atomic number and since all the isotopes of an element have the same atomic number, these are assigned only one position.

### **■** Description of the Modern Periodic Table

The main characteristics of the modern periodic table are,

- (i) The modern periodic table consists of nine vertical columns called 'groups' and seven horizontal rows called 'periods'. The nine groups are marked from 0 to VIII. The groups I to VII are divided each into subgroups A and B. The groups I to VII are termed normal groups. In the VIII group in one place, there are three similar elements placed together which are known as transition triads—Fe, Co and Ni; Ru, Rh and Pd; Os, Ir and Pt; Hs(Uno), Mt (Une) and Uun.
- (ii) Starting from hydrogen to the heaviest element, uranium, there are 92 elements which are arranged in different periods as follows:

_		
First period	2 elements	(very short period)
Second period	8 elements	(short period)
Third period	8 elements	(short period)
Fourth period	18 elements	(long period)
Fifth period	18 elements	(long period)
Sixth period	32 elements	(very long period)
Seventh period	6 elements upto	(very long period, incom-
	at. no. 92	plete period)

The IV, V and VI periods possess two horizontal rows each, which are termed even and odd series. In the 6th period, fifteen elements from lanthanum (At. no. 57) to lutetium (At. no. 71) are given only one position in third group. These

elements are known as rare-earths or lanthanides (from At. no. 58 to 71) and are separately arranged below the table in a horizontal row.

The last period consists of 28 elements, out of which 14 elements from atomic number 90 to 103 are separately arranged like lanthanides below the table in a horizontal row. These elements are called **actinides**.

(iii) Every period starts from a member of alkali group and ends with a member of zero group. The first period, however, starts with hydrogen.

Period	Ist element/ At. no.		ement/ no.		elements period
1st period	H-(1)	. I	He (2)		2
2nd period	Li (3) $\right\}^2$	N	e (10)		8
3rd period	Na (11) $\}^8$	A 8	ır (18)		8
4th period	K (19)	•	(36)		18
5th period	Rb(37)	x را	(e (54)		18
6th period	Cs(55)	,	Rn(86)	•	32
7th period	Fr(87)	}32 Uud	o(118)		nplete I today

The difference in the atomic numbers of subsequent alkali metals indicates that similar properties recur after the intervals of 2, 8, 8, 18, 18 and 32.

(iv) There is a gradual change in properties of the elements, when we move in a period from one end to the other end. Some examples are given below to justify this gradual change.

(a) Valency: Valency of the elements increases from 1 to 7 from left to right if oxygen is taken as standard. The valency of the elements with respect to hydrogen increases from 1 to 4 and then decreases from 4 to 1 in a period.

Group	I	II	III	IV	V	VI	VII
Valency with respect to oxygen	1	2	3	4	5	6	7
Formula of the oxide	$R_2O$	RO	$R_2O_3$	$RO_2$	$R_2O_5$	$RO_3$	$R_2O_7$
Valency with respect to hydrogen	1	2	3	4	3	2	1
Formula of the hydride	e RH	RH <sub>2</sub>	$RH_3$	$RH_4$	$RH_3$	$RH_2$	RH

This trend is observed in every period. Considering the members of third period,

Thus, group number signifies the valency of the elements belonging to that group if oxygen is taken as a standard. **(b) Metallic nature:** In a period from left to right metallic nature decreases while non-metallic character increases.

3rd period Na Mg Al Si P S Cl

Metals Metalloid Non-metals

Non-metallic nature in increasing order

Metallic nature in decreasing order

(c) Electropositive / Electronegative character: The electropositive character decreases in a period from left to right or electronegative character increases.

2nd period Li Be B C N O F

Electronegative nature in increasing order

or

Electropositive nature in decreasing order

(d) Oxidising and reducing nature: In a period, from left to right, the reducing nature decreases while oxidising nature increases.

3rd period Na Mg Al Si P S Cl
Strong reducing agents Strong oxidising agents

**(e)** Nature of oxides: In a period, from left to right the basic nature of the oxides decreases while acidic nature of the oxides increases.

 $Na_2O$  is more basic than MgO and MgO is more basic than  $Al_2O_3$ .

**(v) Typical elements:** The elements of second and third periods are called **typical elements** as they summarise the properties of their respective groups.

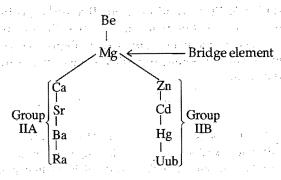
 Groups
 I
 II
 III
 IV
 V
 VI
 VII

 2nd period
 Li
 Be
 B
 C
 N
 O
 F

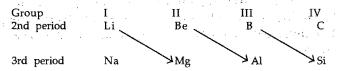
 3rd period
 Na
 Mg
 Al
 Si
 P
 S
 Cl

Li and Na are typical elements of 1st group while Be and Mg are typical elements of 2nd group and so on.

(vi) Bridge elements: The typical elements of third period are also called bridge elements as the division between two subgroups A and B starts from these elements. In second group, Mg acts as a bridge element. The properties of bridge element are somewhat mixed properties of the elements of two subgroups as magnesium shows similarities with alkaline earth metals (IIA) on one hand and with zinc metals (IIB) on the other.



(vii) Diagonal relationship: The first three members of second period (Li, Be and B) not only show similarities with the members of their own groups but show similarities with the elements diagonally placed in the higher groups. This resemblance is termed diagonal relationship.



Lithium shows similarities with magnesium, beryllium with aluminium and boron with silicon.

(viii) The elements belonging to the same subgroup exhibit either same properties or a regular gradation in properties from top to bottom. Some examples are given below:

- (a) In the case of elements of IA group (Li, Na, K, Rb, Cs), the electropositive character or reactivity increases as the atomic number increases. All the members show monovalency and are never found in free state. The oxides are basic and form strong alkalies.
- (b) In IVA group, the metallic character increases gradually:

The acidic nature of the oxides decreases from top to bottom. CO<sub>2</sub> is acidic while PbO<sub>2</sub> is basic in nature.

(c) In VIIA group, the reactivity of the halogens decreases from top to bottom. These are electronegative and this nature decreases from top to bottom. Their hydrides are acidic in nature and acidic nature increases as the atomic number increases.

(ix) The elements of the same subgroup resemble, quite closely to each other but there is hardly any resemblance between the elements of two subgroups A and B. For example, in the first group, the subgroup A consists of alkali metals

(Li, Na, K, Rb, Cs) and subgroup B consists of **coinage metals** (Cu, Ag, Au) but there appears hardly any resemblance between the members of these two subgroups except all show monovalency. Some properties are given below to justify this statement:

IA (alkali metals)
(Li, Na, K, Rb, Cs)
(Cu, Ag, Au)

(i) Soft metals
(ii) Low densities
(iii) Low melting points
(iv) Highly reactive
(v) Never found free in
nature

IB (coinage metals)
(Cu, Ag, Au)

(ii) Hard metals
(iii) High densities
(iii) High melting points
(iv) Less reactive, noble metals
(v) Found mainly free in nature

(vi) Decompose water readily

(vi) Do not decompose water

The difference in properties of two subgroups is maximum in the first group and decreases from first to fourth group. The difference again becomes maximum in the seventh group.

### Applications or Advantages of the Modern Periodic Table

- (i) Classification of elements: There is no doubt that the Mendeleev's periodic system is far superior to the all earlier classifications of elements. The periodic table has reduced the study of 117 known elements into the study of few groups. If we know the properties of a single member of a group, we can have good approximation of the properties of other members of this group without individually studying them.
- (ii) Discovery of new elements: A number of gaps were left in Mendeleev's periodic table for unknown elements. Mendeleev even predicted the properties of these unknown elements. These properties helped the workers to discover the unknown elements more readily and accurately. Thus, the periodic system hastened the discovery of many new elements. In modern periodic table, no gap is present, *i.e.*, all the unknown elements upto 112 have been discovered. Recently, the elements with atomic numbers 113 to 116 and 118 have been reported. Element with atomic number 117 is still to be discovered to complete the last, *i.e.*, 7th period of the periodic table.
- (iii) Correction of atomic mass: Atomic mass of an element is related with equivalent mass of the element by the following formula:

Atomic mass = Equivalent mass × valency

Valency of the element can be known from its position in the periodic table. This formula was utilised in the correction of atomic mass of many elements. For example, when Mendeleev presented the periodic table, the atomic mass of beryllium was not correctly known. However, its equivalent mass was known to be 4.55. It was thought that the element possessed valency 3 as its oxide was isomorphous with alumina ( $Al_2O_3$ ). Thus, the atomic mass of this element came out to be  $3 \times 4.55 = 13.65$ . On the basis of this value of atomic mass, it should have been given position after carbon (At. wt. 12) but Mendeleev assigned position to beryllium in second group, *i.e.*, he considered beryllium as bivalent. The atomic mass of beryllium was given the value  $4.55 \times 2 = 9.10$ . This value of atomic mass justified its position in second group along with Mg, Ca, Sr, etc. In the modern periodic table the atomic masses of all the elements have been corrected.

Thus, the (ii) and (iii) points are of only historical importance because all the unknown elements have already been discovered and the atomic masses of the elements have already been corrected.

#### **■** Defects of Modern Periodic Table

Inspite of its great usefulness in the study of various elements, the modern periodic table suffers from the following defects:

- (i) Position of hydrogen: On account of the dual nature of hydrogen as it shows resemblance with alkali metals and also with halogens, its position in periodic table is uncertain. It is sometimes placed in the first group and sometimes in the seventh group. However, the symmetry of the periodic table is not disturbed whether it is accommodated in the first group or in seventh group. It is, therefore, difficult even at present, to decide to where it should correctly be placed.
- (ii) Similar elements separated: Certain elements which show similar properties have been separated in the periodic table. For example, Ba and Pb resemble each other in so many respects but have been placed in second and fourth groups, respectively. Similarly Ag and Tl having similar properties have been separated, Ag placed in the first group and Tl in the third group.
- (iii) Dissimilar elements placed together in the same group: Elements showing marked dissimilarities are placed in one group. For example, coinage metals (Cu, Ag and Au) have been placed with alkali metals in the first group. Manganese has been placed in seventh group along with halogens with which it shows little resemblance.
- (iv) Metals and nonmetals: No attempt has been made to place metals and nonmetals separately in the periodic table. Most of the groups are mixed groups consisting of metals, nonmetals and metalloids.
- (v) Position of VIII group: There are twelve elements in this group and they are accommodated in only four available positions. This group is present between seventh and zero groups which is not justified.
- (vi) Positions of transition elements: Mendeleev regarded only the three triads of VIII group as the only

transition elements but modern studies have confirmed that there are 40 (upto At. no. 112) transition elements. These similar elements are scattered in whole of the periodic table. These elements are present in every group except zero group.

(vii) Position of lanthanides and actinides: Inspite of the fact that members of lanthanide series and actinide series have different atomic numbers, these have not been given individual places in the periodic table. The 14 members of lanthanide series have been placed along with lanthanum in the third group and sixth period and similarly 14 members of the actinide series have been placed along with actinium in third group and seventh period. The justification for assigning one place to these elements has been given on the basis of their similar properties. The properties are so similar that the fifteen elements from La to Lu can be considered as equivalent to one element. In case, these elements are assigned different positions, i.e., arranged in order of their increasing atomic numbers, the symmetry of the whole arrangement would be disrupted. The same explanation can be given in the case of actinides.

# 1.5 NAMING THE ELEMENTS

Every element has been given a definite name and for covenience a nick name which in chemical language is called a **symbol**. When a new element is discovered, the discoverer usually gets the opportunity to suggest a name for the element, which is then approved by **The International Union of Pure and Applied Chemistry-IUPAC**.

Symbols have been derived either by taking the first alphabet of the name of the element or by taking the first alphabet and one more alphabet from the name of the element (for example, C for carbon; N for nitrogen; O for oxygen; Ca for calcium; Al for aluminium, etc.) but there are quite number of elements for which the derivation of the symbol is not quite so obvious: for example, Na for sodium; Pb for lead; Ag for silver; Fe for iron, etc. Such anomalies occur because of the way, the elements were originally named. Some of the elements were given names in other languages such as Latin, German, etc.

Of all the elements on the periodic table, C,S, Fe, Cu, As, Ag, Sn, Sb, Au, Hg, Pb and Bi were known to ancient civilisations so the date of their 'discovery' is not known. Of these, Fe, Cu,

#### SCIENTIST/PERSONS AFTER WHOM ELEMENTS HAVE BEEN NAMED

Name	Brief biography	Element named
Vasilii Yefrafovich von     Samarski-Bykhovets (1803-1870)	Chief of staff of the Russian Corps of Mining Engineers	samarium, Sm (element 62)
2. Johan Gadolin (1760-1852)	Finnish chemist; first person to isolate a lanthanide element	gadolinium, Gd (element 64)
3. Pierre Curie (1859-1906) and Marie Curie (1867-1934)	Husband and wife scientific team; Pierre French and Marie Polish by birth; jointly won the Nobel Prize in physics in 1903	curium, Cm (element 96)
4. Albert Einstein (1879-1955)	Most famous scientist of the twentieth century; German by birth; won the Nobel Prize in physics in 1921	einsteinium, Es (element 99)
5. Enrico Fermi (1901-1954)	Italian physicist; made great advances in the study of nuclear reactions; won the Nobel Prize in physics in 1938	fermium, Fm (element 100)
6. Dmitri Mendeleev (1834-1907)	Russian chemist; renowned for the development of the periodic table	mendelevium, Md (element 101)
7. Alfred Nobel (1833-1896)	Swedish inventor of dynamite an patron of the Nobel Prizes	nobelium, No (element 102)
8. Ernest Lawrence (1901-1958)	American inventor of the cyclotron; won the Nobel Prize in physics in 1939	lawrencium, Lr (element 103)
9. Ernest Rutherford (1871-1937)	New Zealand physicist/chemist; made seminal contributions to understanding the structure of the atom; won the Nobel Prize in chemistry in 1908	rutherfordium, Rf (element 104)
10. Glenn Seaborg (1912-1999)	American chemist; first prepared many of the elements beyond uranium in the periodic table; won the Nobel Prize in chemistry in 1951	seaborgium, Sg (element 106)
11. Niels Bohr (1885-1962)	Danish physicist; studied electronic energy levels within atoms, which help our understanding of the atom; won the Nobel Prize in physics in 1922	bohrium, Bh (element 107)
12. Lise Meitner (1878-1968)	Austrian physicist; made discoveries concerning nuclear fission; controversially never awarded a Nobel Prize	meitnerium, Mt (element 109)
13. Wilhelm Röntgen (1845-1923)	German physicist; discoverer of X-rays; won the Nobel Prize in physics in 1901	röntgenium, Rg (element 111)

Ag, Sn, Sb, Au, Hg and Pb are the abbreviations for the Latin names ferrum, cuprum, argentum, stannum, stibium, aurum, hydragyrum and plumbum. The earliest known discovery of an element was that of phosphorus, P. It was isolated in 1669 by Hennig Brand from the distillation of urine (he was apparently trying to make silver or gold—unsuccessfully, of course!) and was named after the Greek word phosphoros, meaning 'bringer of light', as the element glows in the dark. Elements have been named after countries (germanium, francium, americium, polonium) and even after the places they were first discovered; the Swedish town of Ytterby has the distinction of having four elements (erbium, Er; ytterbium, Yb; yttrium, Y; and terbium, Tb) named after it, as these were found in deposits close to the town. Surprisingly few elements have been named after people; at present, only 14 people have been immortalised on the periodic table, and they are listed in table given on page 9.

# ■ Nomenclature of Elements with Atomic Numbers > 100

The elements coming after uranium which do not exist naturally, are named transuranic or transuranium elements. The elements with Z = 104 - 116 and 118 have been reported recently and are called transactinides or super-heavy elements. These are synthetic, i.e., man-made elements. The production of synthetic elements requires binuclear reactions between two positive nuclei that must be fused together against the force of electrical repulsion. Nuclear accelerators are used for this purpose. There are currently two major groups working on producing super-heavy elements, one in California, USA and the other at Dubna near Moscow, Russia. By convention, the workers who discover a new element have the right to name it. However, in recent years, on account of competitive spirit disputes have arisen over the names of the newly discovered elements. For example, both American and Russian scientists claimed credit for the discovery of the element 104. The Americans named it Rutherfordium whereas Russians named it Kurchatovium. To avoid such problems, the IUPAC suggested that until the discovery of the new element is proved and its name is officially recognised, a systematic nomenclature based on the atomic number of the element be followed. The following are the points of the nomenclature of the element having atomic

1. The names are derived by using the numerical roots for three digits in the atomic number of the element and adding the ending -ium. The roots for the numbers are:

Digit	Name	Abbreviation
0	nil	<b>n</b>
		$oldsymbol{u}_{i,j}$
2	bi	b
3	tri	
4	quad	
5		<b>p</b>
6		grand holder between
	sept	and the state of t
		tax aro, txt. to a
s, it ,	enn	. Units e who we

- 2. In certain cases the names are shortened. For example, 'biium' and 'triium' are shortened to 'bium' and 'trium' and 'ennnil' is shortened to 'ennil'.
- 3. The symbol for the element is made up from the first letters from the roots which make up the names. The mixture of Latin and Greek roots has been chosen to ensure that the symbols are all different.

**IUPAC Nomenclature for the Super Heavy-Elements** 

Atomic number	Name of t	the element	Symbol
101	Unnilunium	$\frac{\underline{Un} - \underline{nil} - \underline{un} - ium}{1}$	(Unu)
102	Unnilbium	$\frac{\operatorname{Un}}{1} - \frac{\operatorname{nil}}{0} - \frac{\operatorname{bi}}{2} - \operatorname{um}$	(Unb)
103		$\frac{Un}{1} - \frac{nil}{0} - \frac{tri}{3} - um$	(Unt)
104	Unnilquadium	$\frac{\operatorname{Un} - \operatorname{nil}}{1} - \frac{\operatorname{quad}}{0} - \operatorname{ium}$	(Unq)
105	Unnilpentium	* *	(Unp)
106	Unnilhexium		(Unh)
107	Unnilseptium		(Uns)
108	Unniloctium		(Uno)
109	Unnilennium		(Une)
110	Ununnilium		(Uun)
111	Unununium	$\frac{Un}{1} - \frac{un}{1} - \frac{nu}{1} - ium$	(Uuu)
112	Ununbium	$\frac{Un}{1} - \frac{un}{1} - \frac{bi}{2} - um$	(Uub)
113	Ununtrium	$\frac{Un}{1} - \frac{un}{1} - \frac{tri}{3} - um$	(Uut)
114	Ununquadium	$\frac{Un}{1} - \frac{un}{1} - \frac{quad}{4} - ium$	(Uuq)
115	Ununpentium	$\frac{Un}{1} - \frac{un}{1} - \frac{pent}{5} - ium$	(Uup)
116	Ununhexium	$\frac{\text{Un}}{1} - \frac{\text{un}}{1} - \frac{\text{hex}}{6} - \text{ium}$	(Uuh)
118	Ununoctium	$\frac{\text{Un}}{1} - \frac{\text{un}}{1} - \frac{\text{oct}}{8} - \text{ium}$	(Uuo)
120	Unbinilium	$\frac{U\mathbf{n}}{1} - \frac{\mathbf{bi}}{2} - \frac{\mathbf{nil}}{0} - \mathbf{ium}$	(Ubn)

At present 117 elements have been discovered. These are the elements with atomic numbers upto 116 and 118. Element

with atomic number 117 is yet to be discovered. Official IUPAC names for the elements upto 111 have been approved by the Commission on Nomenclature of Inorganic Chemistry (CNIC).

Thus, the newly discovered element is first given a temporary name on the basis of atomic number and later on a permanent name with symbol is alloted by the consent of IUPAC representatives.

### Nomenclature of Elements with Atomic Number above 100

Atomic number	Name on the basis of atomic number (Temporary)	Official IUPAC name (Permanent)	Symbol
101	Unnilunium	Mendelevium	Md
102	Unnilbium	Nobelium	No
103	Unniltrium	Lawrencium	Lr
104	Unnilquadium	Rutherfordium	Rf
105	Unnilpentium	Dubnium	Db
106	Unnilhexium	Seaborgium	Sg
107	Unnilseptium	Bohrium	Bh
108	Unniloctium	Hassium	Hs
109	Unnilennium	Meitnerium	Mt
110	Ununnilium	Darmstadtium	Ds
111	Unununium	Rontgenium	Rg
112	Ununbium*		
113	Ununtrium*		_
114	Ununquadium*		
115	Ununpentium*		
116	Ununhexium*		
118	Ununoctium*		

<sup>\*</sup>Official IUPAC name yet to be announced.

# 1.6 ELECTRONIC CONFIGURATIONS AND THE PERIODIC TABLE

The aufbau principle and electronic configuration of the atoms of elements provide a theoretical foundation for the classification of elements. It is now recognised that the periodic table is essentially the consequence of the periodic variation in electronic configuration of the atoms of the elements which determine the physical and chemical properties of the elements and their compounds. The elements in a vertical column, i.e., in a group of the periodic table exhibit similar chemical behaviour. This is due to the fact that these elements have same number and same distribution of electrons in their outermost orbitals, i.e., in the valency shell. For example, the group IA elements (alkali metals) which show same chemical behaviour possess same valence shell configuration, i.e., ns<sup>1</sup>. Similarly, the group VIIA elements (halogens) which are similar in chemical properties possess same valence shell configuration, ns<sup>2</sup>np<sup>5</sup>.

In the periodic table, the elements have been arranged in order of increasing atomic number, *i.e.*, increased number of orbital electrons. Thus, each element contains one more orbital electron than the preceding element. Each period starts with  $ns^1$  configuration and ends with a noble gas (He,  $1s^2$ , in the first period and  $ns^2np^6$  configuration with rest of the elements). The sequence in which the various energy levels are filled determines the number of elements.

1st period	1s		M pr	2 elements in this period
2nd period	2s		2p	8 elements in this period
3rd period	3s		3p	8 elements in this period
4th period	<b>4</b> s	3 d	4 p	18 elements in this period
5th period	5s	4 <i>d</i>	5 <i>p</i>	18 elements in this period
6th period	6s 4	f 5d	6p .	32 elements in this period
7th period	7s. 5	f 6d	7 p	32 elements in this period

The ground state electronic configurations of the elements are given in the following table. For the sake of simplicity, condensed electronic configurations of the elements are given. In writing condensed electronic configuration of an element, the electronic configuration of the nearest noble gas of lower atomic number is represented by its chemical symbol in square bracket. For example, the condensed electronic configuration of sodium can be written as:

 $\label{eq:Nellows} \mbox{[Ne] } 3s^1$  Electronic Structures of the Elements

Z	Element	Symbol	Structure
		Period – 1	
1	Hydrogen	Н	$1s^1$
2	Helium	He	1s <sup>2</sup>
		Period - 2	
3	Lithium	Li	[He] 2s <sup>1</sup>
4	Beryllium	Be	[He] $2s^2$
5	Boron	В	[He] $2s^2 2p^1$
6	Carbon	С	[Ho] 2c2 2m2
7	Nitrogen	N	IHel 2c 2n
8	Oxygen	0	[He] $2s^2 2p^4$
9	Fluorine	F	[He] $2s^2 2p^5$
10	Neon	Ne <sup>-</sup>	[He] $2s^2$ $2p^4$ [He] $2s^2$ $2p^5$ [He] $2s^2$ $2p^6$
		Period - 3	
11	Sodium	Na	[Ne] 3s <sup>1</sup>
12	Magnesium	Mg	[Ne] 3s <sup>2</sup>
13	Aluminium	Al	[Ne] $3s^2 3p^1$
14	Silicon	Si	[Ne] $3s^2 3p^2$
15	Phosphorus	P	[Ne] $3s^2 - 3p^3$
16	Sulphur	S	[Ne] $3s^2 3p^4$
17	Chlorine	Cl	[Ne] $3s^2 3p^5$
18	Argon	Ar	[Ne] $3s^2 3p^6$
		Period – 4	2
19	Potassium	K	[Ar] 4s <sup>1</sup>
20	Calcium	Ca	$[Ar]$ $4s^2$
21	Scandium	Sc	[Ar] $3d^1 + 4s^2$
22	Titanium	Ti	[Ar] $3d^2 + 4s^2$
23	Vanadium *	V	$[Ar] 3d^3 4s^2$

Z	Element	Symbol	Structure
24	Chromium	Cr	[Ar] $3d^5   4s^1$
25	Manganese	Mn	[Ar] $3d^5 4s^2$
26	Iron	Fe	[Ar] $3d^6   4s^2$
27	Cobalt	Co	[Ar] $3d^7   4s^2$
28	Nickel	Ni	[Ar] $3d^8   4s^2$
29	Copper.	Cu-	[Ar] $3d^{10}$ $4s^1$
30	Zinc	Zn	[Ar] $3d^{10}$ $4s^2$
31	Gallium	Ga	[Ar] $3a^{10}$ $4s^2$ $4p^1$
32	Germanium	Ge	[Ar] $3d^{10}$ $4s^2$ $4p^2$
33	Arsenic	As	[Ar] $3d^{10}$ $4s^2$ $4p^3$
34	Selenium	Se	[Ar] $3d^{10}$ $4s^2$ $4p^4$
35	Bromine	Br	[Ar] $3d^{10}$ $4s^2$ $4p^5$
36	Krypton	Kr	[Ar] $3d^{10}$ $4s^2$ $4p^6$
,		eriod – 5	[11] 04 15 19
37		Rb	[Kr] 5s <sup>1</sup>
	Rubidium	Sr	[Kr] 5s
38	Strontium		
39	Yttrium	Υ	[Kr] $4d^1   5s^2$
40	Zirconium	Zr	[Kr] $4d^2   5s^2$
41	Niobium	Nb	[Kr] $4d^4$ $5s^1$
42	Molybdenum	Mo	[Kr] $4d^5   5s^1$
43	Technetium	Tc	[Kr] $4d^5$ $5s^2$
		Tc	[Kr] $4d^6$ $5s^1$
44	Ruthenium	Ru	[Kr] $4d^7$ $5s^1$
45	Rhodium	Rh	[Kr] $4d^8$ $5s^1$
46	Palladium	Pd	[Kr] $4d^{10}$ $5s^0$
47	Silver	Ag	[Kr] $4d^{10}$ $5s^1$
48	Cadmium	Cd	[Kr] $4d^{10}$ $5s^2$
49	Indium	In	[Kr] $4d^{10}$ $5s^2$ $5p^1$
50	Tin .	Sn	[Kr] $4d^{10}$ $5s^2$ $5p^2$
51	Antimony	Sb	[Kr] $4d^{10}$ $5s^2$ $5p^3$
52	Tellurium	Te	[Kr] $4d^{10}$ $5s^2$ $5v^4$
53	Iodine	I	[Kr] $4d^{10}$ $5s^2$ $5p^5$
54	Xenon	Xe	[Kr] $4d^{10}$ $5s^2$ $5p^6$
	1	Period - 6	
55	Caesium	Cs	[Xe] 6s1
56	Barium	Ba	[Xe] 6s <sup>2</sup>
E 7	Lanthanum	T a	[Xe] $5d^1$ $6s^2$
57		La	
58	Cerium	Ce	[Xe] $4f^1   5d^1   6s^2$
59	Praseodymium	Pr	[Xe] $4f^3$ $5d^0$ $6s^2$
60	Neodymium	Nd	[Xe] $4f^4   5d^0   6s^2$
61	Promethium	Pm	[Xe] $4f^5$ $5d^0$ $6s^2$
62	Samarium	Sm	[Xe] $4f^6   5d^0   6s^2$
63	Europium	Eu	[Xe] $4f^7   5d^0   6s^2$
64	Gadolinium	Gd	[Xe] $4f^7$ $5d^1$ $6s^2$
65	Terbium	Tb	[Xe] $4f^9   5d^0   6s^2$
66	Dysprosium	Dy	[Xe] $4f^{10}$ $5d^0$ $6s^2$
67	Holmium	Ho	[Xe] $4f^{11}$ $5d^0$ $6s^2$
68	Erbium	Er	[Xe] $4f^{12}$ $5d^0$ $6s^2$
			[Xe] $4f^{13}$ $5d^0$ $6s^2$
69 70	Thulium	Tm Vh	[Xe] $4f^{-1} 5a^{-1} 6s^{-1}$
70	Ytterbium	Yb	
71	Lutetium	Lu	[Xe] $4f^{14}$ $5d^1$ $6s^2$
72	Hafnium	Hf	[Xe] $4f^{14}$ $5d^2$ $6s^2$
73	Tantalum	Ta	[Xe] $4f^{14}$ $5d^3$ $6s^2$
74	Tungsten	W	[Xe] $4f^{14}$ $5d^4$ $6s^2$
75	Rhenium	Re	[Xe] $4f^{14}$ $5d^5$ $6s^2$
-	,	-	· /

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Z	Element	Symbol	Struc	ture			
177	76	Osmium	Os	[Xe] 4f <sup>14</sup>	$\cdot 5d^6$	$6s^2$		
78         Platinum         Pt         [Xe] $4f^{14}$ $5d^{3}$ $6s^{1}$ 79         Gold         Au         [Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$ 80         Mercury         Hg         [Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$ 81         Thallium         Tl         [Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$ $6p^{2}$ 81         Thallium         Tl         [Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$ $6p^{2}$ 83         Bismuth         Bi         [Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$ $6p^{2}$ 84         Polonium         Po         [Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$ $6p^{6}$ 85         Astatine         At         [Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$ $6p^{6}$ Period – 7           87         Francium         Fr         [Rn] $7s^{2}$ $6d^{1}$ $7s^{2}$ 86         Radon         Rn         [Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$ $6p^{6}$ Period – 7           87         Francium         Rr	77	lridium	lr	[Xe] 4f <sup>14</sup>	$5d^7$	$6s^2$		
The first color	78	Platinum	Pt	[Xe] 4f <sup>14</sup>	$5d^9$	$6s^1$		
Mercury	79	Gold		[Xe] 4f <sup>14</sup>	$5d^{10}$	$6s^1$		
Thallium	80	Mercury	Hg	. [Xe] 4f <sup>14</sup>	$5d^{10}$	$6s^2$		
83       Bismuth       Bi       [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^3$ 84       Polonium       Po       [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^4$ 85       Astatine       At       [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^5$ Period – 7         87       Francium       Fr       [Rn] $7s^1$ $88$ Radium       Ra       [Rn] $7s^2$ 89       Actinium       Ac       [Rn] $6d^2$ $7s^2$ 90       Thorium       Th       [Rn] $6d^2$ $7s^2$ 91       Protactinium       Pa       [Rn] $5f^2$ $6d^1$ $7s^2$ 91       Protactinium       Pa       [Rn] $5f^3$ $6d^1$ $7s^2$ 93       Neptunium       <	81	Thallium		[Xe] 4f <sup>14</sup>	$5d^{10}$	$6s^2$	$6p^1$	
83       Bismuth       Bi $[Xe] 4f^{14} 5d^{10} 6s^2 6p^3$ 84       Polonium       Po $[Xe] 4f^{14} 5d^{10} 6s^2 6p^5$ 85       Astatine       At $[Xe] 4f^{14} 5d^{10} 6s^2 6p^5$ 86       Radon       Rn $[Xe] 4f^{14} 5d^{10} 6s^2 6p^5$ Period - 7         87       Francium       Fr $[Rn] 7s^1$ 88       Radium       Ra $[Rn] 7s^2$ 89       Actinium       Ac $[Rn] 6d^2 7s^2$ 90       Thorium       Th $[Rn] 6d^2 7s^2$ 91       Protactinium       Pa $[Rn] 5f^2 6d^1 7s^2$ 92       Uranium       U $[Rn] 5f^3 6d^1 7s^2$ 93       Neptunium       Np $[Rn] 5f^4 6d^1 7s^2$ 94       Plutonium       Pu $[Rn] 5f^6 6d^0 7s^2$ 95       Americium       Am $[Rn] 5f^7 6d^1 7s^2$ 97       Berkelium $[Rn] 5f^8 6d^1 7s^2$ 98       Californium       Cf $[Rn] 5f^{10} 6d^0 7s^2$ 99       Einsteinium       Es $[Rn] 5f^{10} 6d^0 7s^2$ 100       Fermium       Fm $[Rn] 5f^{14} 6d^0 7s^2$	82	Lead	Pb	[Xe] 4f <sup>14</sup>	$5d^{10}$	$6s^2$	$6p^2$	
84       Polonium       Po       [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^4$ 85       Astatine       At       [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^5$ Period - 7         Period - 7 <th colsp<="" td=""><td>83</td><td>Bismuth</td><td>Bi</td><td>[Xe] 4f<sup>14</sup></td><td><math>5d^{10}</math></td><td></td><td><math>6p^3</math></td></th>	<td>83</td> <td>Bismuth</td> <td>Bi</td> <td>[Xe] 4f<sup>14</sup></td> <td><math>5d^{10}</math></td> <td></td> <td><math>6p^3</math></td>	83	Bismuth	Bi	[Xe] 4f <sup>14</sup>	$5d^{10}$		$6p^3$
Radon   Rn   [Xe] 4f <sup>14</sup>   5d <sup>10</sup>   6s <sup>2</sup>   6p <sup>5</sup>	84	Polonium	Po	[Xe] 4f <sup>14</sup>	$5d^{10}$		$6p^4$	
Radon   Rn   [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>6</sup>	85	Astatine	At	[Xe] 4f <sup>14</sup>	$5d^{10}$	$6s^2$	$6p^5$	
87       Francium       Fr $[Rn] 7s^1$ 88       Radium       Ra $[Rn] 7s^2$ 89       Actinium       Ac $[Rn] 6d^1 7s^2$ 90       Thorium       Th $[Rn] 6d^2 7s^2$ 91       Protactinium       Pa $[Rn] 5f^2 6d^1 7s^2$ 91       Protactinium       Pu $[Rn] 5f^3 6d^1 7s^2$ 92       Uranium       U $[Rn] 5f^3 6d^1 7s^2$ 93       Neptunium       Np $[Rn] 5f^4 6d^1 7s^2$ 94       Plutonium       Pu $[Rn] 5f^6 6d^0 7s^2$ 95       Americium       Am $[Rn] 5f^7 6d^0 7s^2$ 96       Curium       Cm $[Rn] 5f^7 6d^0 7s^2$ 97       Berkelium $\begin{cases} Bk & [Rn] 5f^3 6d^0 7s^2 \\ Bk & [Rn] 5f^3 6d^0 7s^2 \end{cases}$ 98       Californium       Cf $[Rn] 5f^{10} 6d^0 7s^2$ 99       Einsteinium       Es $[Rn] 5f^{11} 6d^0 7s^2$ 101       Mendelevium       Md $[Rn] 5f^{12} 6d^0 7s^2$ 102       Nobelium       No $[Rn] 5f^{14} 6d^0 7s^2$ 103       Lawrencium       Rf $[Rn] 5f^{14} 6d^0 7s^2$ 105       D	86	Radon	Rn	[Xe] 4f <sup>14</sup>	5d <sup>10</sup>	6s <sup>2</sup>	6p <sup>6</sup>	
88       Radium       Ra       [Rn] $7s^2$ 89       Actinium       Ac       [Rn] $6d^1$ $7s^2$ 90       Thorium       Th       [Rn] $6d^2$ $7s^2$ 91       Protactinium       Pa       [Rn] $5f^2$ $6d^1$ $7s^2$ 91       Protactinium       Pa       [Rn] $5f^3$ $6d^1$ $7s^2$ 92       Uranium       U       [Rn] $5f^3$ $6d^1$ $7s^2$ 93       Neptunium       Np       [Rn] $5f^4$ $6d^0$ $7s^2$ 94       Plutonium       Pu       [Rn] $5f^6$ $6d^0$ $7s^2$ 95       Americium       Am       [Rn] $5f^7$ $6d^0$ $7s^2$ 96       Curium       Cm       [Rn] $5f^7$ $6d^0$ $7s^2$ 97       Berkelium $\begin{cases} Bk & [Rn] 5f^8 & 6d^1 & 7s^2 \\ Bk & [Rn] 5f^8 & 6d^1 & 7s^2 \end{cases}$ 98       Californium       Cf       [Rn] $5f^{10}$ $6d^0$ $7s^2$ 99       Einsteinium       Es       [Rn] $5f^{11}$ $6d^0$ $7s^2$ 100       Fermium       Fm       [Rn] $5f^{11}$ $6d^0$ $7s^2$ 101       Mendelevium       Md       [Rn] $5f^{11}$ $6d^0$ $7s^2$ 102       Nobelium       No       [Rn] $5f^{11}$ $6d^0$ $7s^2$ 103       Lawrencium       Lr       [Rn]			Period - 7					
89       Actinium       Ac       [Rn] $6d^1$ $7s^2$ 90       Thorium       Th       [Rn] $6d^2$ $7s^2$ 91       Protactinium       Pa       [Rn] $5f^2$ $6d^1$ $7s^2$ 91       Protactinium       Pa       [Rn] $5f^3$ $6d^1$ $7s^2$ 92       Uranium       U       [Rn] $5f^3$ $6d^1$ $7s^2$ 93       Neptunium       Np       [Rn] $5f^4$ $6d^1$ $7s^2$ 94       Plutonium       Pu       [Rn] $5f^6$ $6d^0$ $7s^2$ 95       Americium       Am       [Rn] $5f^7$ $6d^0$ $7s^2$ 96       Curium       Cm       [Rn] $5f^7$ $6d^0$ $7s^2$ 97       Berkelium $\begin{cases} Bk & [Rn] 5f^8$ $6d^0$ $7s^2$ 98       Californium       Cf       [Rn] $5f^{10}$ $6d^0$ $7s^2$ 99       Einsteinium       Es       [Rn] $5f^{11}$ $6d^0$ $7s^2$ 100       Fermium       Fm       [Rn] $5f^{12}$ $6d^0$ $7s$	87	Francium	Fr	[Rn] $7s^1$				
90       Thorium       Th $[Rn]$ $6d^2$ $7s^2$ 91       Protactinium       Pa $[Rn]$ $5f^2$ $6d^1$ $7s^2$ 92       Uranium       U $[Rn]$ $5f^3$ $6d^1$ $7s^2$ 93       Neptunium       Np $[Rn]$ $5f^4$ $6d^1$ $7s^2$ 94       Plutonium       Pu $[Rn]$ $5f^6$ $6d^0$ $7s^2$ 95       Americium       Am $[Rn]$ $5f^7$ $6d^0$ $7s^2$ 96       Curium       Cm $[Rn]$ $5f^7$ $6d^0$ $7s^2$ 97       Berkelium $\begin{bmatrix} Bk & [Rn] \\ 5f^9 & 6d^0 \\ 7s^2 \\ \end{bmatrix}$ $6d^0$ $7s^2$ 98       Californium       Cf $[Rn]$ $5f^{10}$ $6d^0$ $7s^2$ 98       Californium       Es $[Rn]$ $5f^{11}$ $6d^0$ $7s^2$ 99       Einsteinium       Es $[Rn]$ $5f^{11}$ $6d^0$ $7s^2$ 100       Fermium       Fm $[Rn]$ $5f^{12}$ $6d^0$ $7s^2$ 102       <	88	Radium	Ra	[Rn] 7s <sup>2</sup>				
90       Thorium       Th $[Rn]$ $6d^2$ $7s^2$ 91       Protactinium       Pa $[Rn]$ $5f^2$ $6d^1$ $7s^2$ 92       Uranium       U $[Rn]$ $5f^3$ $6d^1$ $7s^2$ 93       Neptunium       Np $[Rn]$ $5f^4$ $6d^1$ $7s^2$ 94       Plutonium       Pu $[Rn]$ $5f^6$ $6d^0$ $7s^2$ 95       Americium       Am $[Rn]$ $5f^7$ $6d^0$ $7s^2$ 96       Curium       Cm $[Rn]$ $5f^7$ $6d^0$ $7s^2$ 97       Berkelium $\begin{bmatrix} Bk & [Rn] \\ 5f^9 & 6d^0 \\ 7s^2 \\ \end{bmatrix}$ $6d^0$ $7s^2$ 98       Californium       Cf $[Rn]$ $5f^{10}$ $6d^0$ $7s^2$ 98       Californium       Es $[Rn]$ $5f^{11}$ $6d^0$ $7s^2$ 99       Einsteinium       Es $[Rn]$ $5f^{11}$ $6d^0$ $7s^2$ 100       Fermium       Fm $[Rn]$ $5f^{12}$ $6d^0$ $7s^2$ 102       <	89	Actinium	Ac	[Rn]	$6d^1$	$7s^2$		
92         Uranium         U         [Rn] $5f^3$ $6d^1$ $7s^2$ 93         Neptunium         Np         [Rn] $5f^4$ $6d^1$ $7s^2$ 94         Plutonium         Pu         [Rn] $5f^6$ $6d^0$ $7s^2$ 95         Americium         Am         [Rn] $5f^7$ $6d^0$ $7s^2$ 96         Curium         Cm         [Rn] $5f^7$ $6d^1$ $7s^2$ 97         Berkelium         Bk         [Rn] $5f^9$ $6d^0$ $7s^2$ 98         Californium         Cf         [Rn] $5f^{10}$ $6d^0$ $7s^2$ 99         Einsteinium         Es         [Rn] $5f^{11}$ $6d^0$ $7s^2$ 100         Fermium         Fm         [Rn] $5f^{12}$ $6d^0$ $7s^2$ 101         Mendelevium         Md         [Rn] $5f^{13}$ $6d^0$ $7s^2$ 102         Nobelium         No         [Rn] $5f^{14}$ $6d^0$ $7s^2$ 103         Lawrencium         Lr         [Rn] $5f^{14}$ $6d^0$ $7s^2$ 104         Rutherfordium         Rf         [Rn] $5f^{14}$ $6d^0$ $7s^2$ 105         Dubnium         Db         [Rn] $5f^{14}$ $6d^3$ $7s^2$ 106         Seaborgium         Sg         [Rn] $5f^{14}$ $6d^3$ $7s^2$ 108         Hassnium         Hs <td>90</td> <td>Thorium</td> <td>Th</td> <td>[Rn]</td> <td><math>6d^2</math></td> <td><math>7s^2</math></td> <td></td>	90	Thorium	Th	[Rn]	$6d^2$	$7s^2$		
93       Neptunium       Np       [Rn] $5f^4$ $6d^1$ $7s^2$ 94       Plutonium       Pu       [Rn] $5f^6$ $6d^0$ $7s^2$ 95       Americium       Am       [Rn] $5f^7$ $6d^0$ $7s^2$ 96       Curium       Cm       [Rn] $5f^7$ $6d^1$ $7s^2$ 97       Berkelium       Bk       [Rn] $5f^9$ $6d^0$ $7s^2$ 98       Californium       Cf       [Rn] $5f^{10}$ $6d^0$ $7s^2$ 99       Einsteinium       Es       [Rn] $5f^{11}$ $6d^0$ $7s^2$ 100       Fermium       Fm       [Rn] $5f^{12}$ $6d^0$ $7s^2$ 101       Mendelevium       Md       [Rn] $5f^{12}$ $6d^0$ $7s^2$ 102       Nobelium       No       [Rn] $5f^{14}$ $6d^0$ $7s^2$ 103       Lawrencium       Lr       [Rn] $5f^{14}$ $6d^0$ $7s^2$ 104       Rutherfordium       Rf       [Rn] $5f^{14}$ $6d^0$ $7s^2$ 105       Dubnium       Db       [Rn] $5f^{14}$ $6d^3$ $7s^2$ 106       Seaborgium       Sg       [Rn] $5f^{14}$ $6d^3$ $7s^2$ 107       Bohrium       Bh       [Rn] $5f^{14}$ $6d^5$ $7s^2$ 108       Hassnium       Hs       [Rn] $5f^{14}$ $6d^5$ $7s^2$ 109       Meitnerium	91	Protactinium	Pa	[Rn] $5f^2$	$6d^1$			
93         Neptunium         Np         [Rn] $5f^4$ $6d^1$ $7s^2$ 94         Plutonium         Pu         [Rn] $5f^6$ $6d^0$ $7s^2$ 95         Americium         Am         [Rn] $5f^7$ $6d^0$ $7s^2$ 96         Curium         Cm         [Rn] $5f^7$ $6d^1$ $7s^2$ 97         Berkelium         Bk         [Rn] $5f^9$ $6d^0$ $7s^2$ 98         Californium         Cf         [Rn] $5f^{10}$ $6d^0$ $7s^2$ 99         Einsteinium         Es         [Rn] $5f^{11}$ $6d^0$ $7s^2$ 100         Fermium         Fm         [Rn] $5f^{12}$ $6d^0$ $7s^2$ 101         Mendelevium         Md         [Rn] $5f^{13}$ $6d^0$ $7s^2$ 102         Nobelium         No         [Rn] $5f^{14}$ $6d^0$ $7s^2$ 103         Lawrencium         Lr         [Rn] $5f^{14}$ $6d^0$ $7s^2$ 104         Rutherfordium         Rf         [Rn] $5f^{14}$ $6d^0$ $7s^2$ 105         Dubnium         Db         [Rn] $5f^{14}$ $6d^3$ $7s^2$ 106         Seaborgium         Sg         [Rn] $5f^{14}$ $6d^3$ $7s^2$ 107         Bohrium         Bh         [Rn] $5f^{14}$ $6d^5$ $7s^2$ 108         Hassnium	92	Uranium	U	[Rn] 5f <sup>3</sup>	$6d^1$	$7s^2$		
95       Americium       Am       [Rn] $5f^7$ $6d^0$ $7s^2$ 96       Curium       Cm       [Rn] $5f^7$ $6d^1$ $7s^2$ 97       Berkelium       Bk       [Rn] $5f^9$ $6d^0$ $7s^2$ 98       Californium       Cf       [Rn] $5f^{10}$ $6d^0$ $7s^2$ 99       Einsteinium       Es       [Rn] $5f^{11}$ $6d^0$ $7s^2$ 100       Fermium       Fm       [Rn] $5f^{12}$ $6d^0$ $7s^2$ 101       Mendelevium       Md       [Rn] $5f^{12}$ $6d^0$ $7s^2$ 102       Nobelium       No       [Rn] $5f^{14}$ $6d^0$ $7s^2$ 103       Lawrencium       Lr       [Rn] $5f^{14}$ $6d^0$ $7s^2$ 104       Rutherfordium       Rf       [Rn] $5f^{14}$ $6d^0$ $7s^2$ 105       Dubnium       Db       [Rn] $5f^{14}$ $6d^3$ $7s^2$ 106       Seaborgium       Sg       [Rn] $5f^{14}$ $6d^3$ $7s^2$ 107       Bohrium       Bh       [Rn] $5f^{14}$ $6d^5$ $7s^2$ 108       Hassnium       Hs       [Rn] $5f^{14}$ $6d^6$ $7s^2$ 109       Meitnerium       Mt       [Rn] $5f^{14}$ $6d^8$ $7s^2$ 110       Darmstadtium       Ds       [Rn] $5f^{14}$ $6d^8$ $7s^2$ 111       Ront	93	Neptunium	Np .	[Rn] 5f <sup>4</sup>	$6d^1$			
95       Americium       Am       [Rn] $5f^7$ $6d^0$ $7s^2$ 96       Curium       Cm       [Rn] $5f^7$ $6d^1$ $7s^2$ 97       Berkelium       Bk       [Rn] $5f^9$ $6d^0$ $7s^2$ 98       Californium       Cf       [Rn] $5f^{10}$ $6d^0$ $7s^2$ 99       Einsteinium       Es       [Rn] $5f^{11}$ $6d^0$ $7s^2$ 100       Fermium       Fm       [Rn] $5f^{12}$ $6d^0$ $7s^2$ 101       Mendelevium       Md       [Rn] $5f^{12}$ $6d^0$ $7s^2$ 102       Nobelium       No       [Rn] $5f^{14}$ $6d^0$ $7s^2$ 103       Lawrencium       Lr       [Rn] $5f^{14}$ $6d^0$ $7s^2$ 104       Rutherfordium       Rf       [Rn] $5f^{14}$ $6d^0$ $7s^2$ 105       Dubnium       Db       [Rn] $5f^{14}$ $6d^3$ $7s^2$ 106       Seaborgium       Sg       [Rn] $5f^{14}$ $6d^3$ $7s^2$ 107       Bohrium       Bh       [Rn] $5f^{14}$ $6d^5$ $7s^2$ 108       Hassnium       Hs       [Rn] $5f^{14}$ $6d^6$ $7s^2$ 109       Meitnerium       Mt       [Rn] $5f^{14}$ $6d^8$ $7s^2$ 110       Darmstadtium       Ds       [Rn] $5f^{14}$ $6d^8$ $7s^2$ 111       Ront	94	Plutonium	Pu	[Rn] 5f <sup>6</sup>	$6d^0$	$7s^2$		
96	95	Americium	Am	[Rn] 5f <sup>7</sup>	$6d^0$	$7s^2$		
97 Berkelium $\begin{cases} Bk & [Rn] \ 5f^9 \ 6d^0 \ 7s^2 \\ Bk & [Rn] \ 5f^8 \ 6d^1 \ 7s^2 \end{cases}$ 98 Californium Cf $[Rn] \ 5f^{10} \ 6d^0 \ 7s^2$ 99 Einsteinium Es $[Rn] \ 5f^{11} \ 6d^0 \ 7s^2$ 100 Fermium Fm $[Rn] \ 5f^{12} \ 6d^0 \ 7s^2$ 101 Mendelevium Md $[Rn] \ 5f^{12} \ 6d^0 \ 7s^2$ 102 Nobelium No $[Rn] \ 5f^{13} \ 6d^0 \ 7s^2$ 103 Lawrencium Lr $[Rn] \ 5f^{14} \ 6d^0 \ 7s^2$ 104 Rutherfordium Rf $[Rn] \ 5f^{14} \ 6d^1 \ 7s^2$ 105 Dubnium Db $[Rn] \ 5f^{14} \ 6d^3 \ 7s^2$ 106 Seaborgium Sg $[Rn] \ 5f^{14} \ 6d^4 \ 7s^2$ 107 Bohrium Bh $[Rn] \ 5f^{14} \ 6d^5 \ 7s^2$ 108 Hassnium Hs $[Rn] \ 5f^{14} \ 6d^6 \ 7s^2$ 109 Meitnerium Mt $[Rn] \ 5f^{14} \ 6d^7 \ 7s^2$ 110 Darmstadtium Ds $[Rn] \ 5f^{14} \ 6d^8 \ 7s^2$ 111 Rontgenium Rg $[Rn] \ 5f^{14} \ 6d^8 \ 7s^2$	96	Curium	Cm	[Rn] 5f <sup>7</sup>	$6d^1$	$7s^2$		
	9 <i>7</i>	Berkelium	∫Bk	[Rn] $5f^9$	$6d^0$			
99 Einsteinium Es [Rn] $5f^{11}$ $6d^0$ $7s^2$ 100 Fermium Fm [Rn] $5f^{12}$ $6d^0$ $7s^2$ 101 Mendelevium Md [Rn] $5f^{13}$ $6d^0$ $7s^2$ 102 Nobelium No [Rn] $5f^{14}$ $6d^0$ $7s^2$ 103 Lawrencium Lr [Rn] $5f^{14}$ $6d^1$ $7s^2$ 104 Rutherfordium Rf [Rn] $5f^{14}$ $6d^2$ $7s^2$ 105 Dubnium Db [Rn] $5f^{14}$ $6d^3$ $7s^2$ 106 Seaborgium Sg [Rn] $5f^{14}$ $6d^3$ $7s^2$ 107 Bohrium Bh [Rn] $5f^{14}$ $6d^4$ $7s^2$ 108 Hassnium Hs [Rn] $5f^{14}$ $6d^6$ $7s^2$ 109 Meitnerium Mt [Rn] $5f^{14}$ $6d^6$ $7s^2$ 110 Darmstadtium Ds [Rn] $5f^{14}$ $6d^8$ $7s^2$ 111 Rontgenium Rg [Rn] $5f^{14}$ $6d^8$ $7s^2$			{ Bk	[Rn] 5f <sup>8</sup>	$6d^1$			
100       Fermium       Fm $[Rn] 5f^{12} 6d^0 7s^2$ 101       Mendelevium       Md $[Rn] 5f^{13} 6d^0 7s^2$ 102       Nobelium       No $[Rn] 5f^{14} 6d^0 7s^2$ 103       Lawrencium       Lr $[Rn] 5f^{14} 6d^1 7s^2$ 104       Rutherfordium       Rf $[Rn] 5f^{14} 6d^2 7s^2$ 105       Dubnium       Db $[Rn] 5f^{14} 6d^3 7s^2$ 106       Seaborgium       Sg $[Rn] 5f^{14} 6d^4 7s^2$ 107       Bohrium       Bh $[Rn] 5f^{14} 6d^5 7s^2$ 108       Hassnium       Hs $[Rn] 5f^{14} 6d^6 7s^2$ 109       Meitnerium       Mt $[Rn] 5f^{14} 6d^8 7s^2$ 110       Darmstadtium       Ds $[Rn] 5f^{14} 6d^8 7s^2$ 111       Rontgenium       Rg $[Rn] 5f^{14} 6d^9 7s^2$	98	Californium	Cf	[Rn] $5f^{10}$	$6d^0$			
101       Mendelevium       Md $[Rn]$ $5f^{13}$ $6d^0$ $7s^2$ 102       Nobelium       No $[Rn]$ $5f^{14}$ $6d^0$ $7s^2$ 103       Lawrencium       Lr $[Rn]$ $5f^{14}$ $6d^1$ $7s^2$ 104       Rutherfordium       Rf $[Rn]$ $5f^{14}$ $6d^2$ $7s^2$ 105       Dubnium       Db $[Rn]$ $5f^{14}$ $6d^3$ $7s^2$ 106       Seaborgium       Sg $[Rn]$ $5f^{14}$ $6d^4$ $7s^2$ 107       Bohrium       Bh $[Rn]$ $5f^{14}$ $6d^5$ $7s^2$ 108       Hassnium       Hs $[Rn]$ $5f^{14}$ $6d^6$ $7s^2$ 109       Meitnerium       Mt $[Rn]$ $5f^{14}$ $6d^8$ $7s^2$ 110       Darmstadtium       Ds $[Rn]$ $5f^{14}$ $6d^8$ $7s^2$ 111       Rontgenium       Rg $[Rn]$ $5f^{14}$ $6d^9$ $7s^2$	99	Einsteinium	Es	[Rn] 5f <sup>11</sup>	$6d^0$			
102       Nobelium       No $[Rn]$ $5f^{14}$ $6d^0$ $7s^2$ 103       Lawrencium       Lr $[Rn]$ $5f^{14}$ $6d^1$ $7s^2$ 104       Rutherfordium       Rf $[Rn]$ $5f^{14}$ $6d^2$ $7s^2$ 105       Dubnium       Db $[Rn]$ $5f^{14}$ $6d^3$ $7s^2$ 106       Seaborgium       Sg $[Rn]$ $5f^{14}$ $6d^4$ $7s^2$ 107       Bohrium       Bh $[Rn]$ $5f^{14}$ $6d^5$ $7s^2$ 108       Hassnium       Hs $[Rn]$ $5f^{14}$ $6d^6$ $7s^2$ 109       Meitnerium       Mt $[Rn]$ $5f^{14}$ $6d^8$ $7s^2$ 110       Darmstadtium       Ds $[Rn]$ $5f^{14}$ $6d^8$ $7s^2$ 111       Rontgenium       Rg $[Rn]$ $5f^{14}$ $6d^9$ $7s^2$	100	Fermium	Fm	[Rn] $5f^{12}$	$6d^0$			
103       Lawrencium       Lr $[Rn]$ $5f^{14}$ $6d^1$ $7s^2$ 104       Rutherfordium       Rf $[Rn]$ $5f^{14}$ $6d^2$ $7s^2$ 105       Dubnium       Db $[Rn]$ $5f^{14}$ $6d^3$ $7s^2$ 106       Seaborgium       Sg $[Rn]$ $5f^{14}$ $6d^4$ $7s^2$ 107       Bohrium       Bh $[Rn]$ $5f^{14}$ $6d^5$ $7s^2$ 108       Hassnium       Hs $[Rn]$ $5f^{14}$ $6d^6$ $7s^2$ 109       Meitnerium       Mt $[Rn]$ $5f^{14}$ $6d^7$ $7s^2$ 110       Darmstadtium       Ds $[Rn]$ $5f^{14}$ $6d^8$ $7s^2$ 111       Rontgenium       Rg $[Rn]$ $5f^{14}$ $6d^9$ $7s^2$	101	Mendelevium	Md	[Rn] $5f^{13}$	$6d^0$			
103       Lawrencium       Lr $[Rn]$ $5f^{14}$ $6d^1$ $7s^2$ 104       Rutherfordium       Rf $[Rn]$ $5f^{14}$ $6d^2$ $7s^2$ 105       Dubnium       Db $[Rn]$ $5f^{14}$ $6d^3$ $7s^2$ 106       Seaborgium       Sg $[Rn]$ $5f^{14}$ $6d^4$ $7s^2$ 107       Bohrium       Bh $[Rn]$ $5f^{14}$ $6d^5$ $7s^2$ 108       Hassnium       Hs $[Rn]$ $5f^{14}$ $6d^6$ $7s^2$ 109       Meitnerium       Mt $[Rn]$ $5f^{14}$ $6d^7$ $7s^2$ 110       Darmstadtium       Ds $[Rn]$ $5f^{14}$ $6d^8$ $7s^2$ 111       Rontgenium       Rg $[Rn]$ $5f^{14}$ $6d^9$ $7s^2$	102	Nobelium	No	[Rn] 5f <sup>14</sup>	$6d^0$			
105       Dubnium       Db $[Rn]$ $5f^{14}$ $6d^3$ $7s^2$ 106       Seaborgium       Sg $[Rn]$ $5f^{14}$ $6d^4$ $7s^2$ 107       Bohrium       Bh $[Rn]$ $5f^{14}$ $6d^5$ $7s^2$ 108       Hassnium       Hs $[Rn]$ $5f^{14}$ $6d^6$ $7s^2$ 109       Meitnerium       Mt $[Rn]$ $5f^{14}$ $6d^7$ $7s^2$ 110       Darmstadtium       Ds $[Rn]$ $5f^{14}$ $6d^8$ $7s^2$ 111       Rontgenium       Rg $[Rn]$ $5f^{14}$ $6d^9$ $7s^2$	103	Lawrencium	Lr	[Rn] 5f <sup>14</sup>	$6d^1$	$7s^2$		
106       Seaborgium       Sg $[Rn]$ $5f^{14}$ $6d^4$ $7s^2$ 107       Bohrium       Bh $[Rn]$ $5f^{14}$ $6d^5$ $7s^2$ 108       Hassnium       Hs $[Rn]$ $5f^{14}$ $6d^6$ $7s^2$ 109       Meitnerium       Mt $[Rn]$ $5f^{14}$ $6d^7$ $7s^2$ 110       Darmstadtium       Ds $[Rn]$ $5f^{14}$ $6d^8$ $7s^2$ 111       Rontgenium       Rg $[Rn]$ $5f^{14}$ $6d^9$ $7s^2$	104	Rutherfordium	Rf .	[Rn] 5f <sup>14</sup>	$6d^2$	$7s^2$		
107       Bohrium       Bh       [Rn] $5f^{14}$ $6d^5$ $7s^2$ 108       Hassnium       Hs       [Rn] $5f^{14}$ $6d^6$ $7s^2$ 109       Meitnerium       Mt       [Rn] $5f^{14}$ $6d^7$ $7s^2$ 110       Darmstadtium       Ds       [Rn] $5f^{14}$ $6d^8$ $7s^2$ 111       Rontgenium       Rg       [Rn] $5f^{14}$ $6d^9$ $7s^2$	105	Dubnium		[Rn] $5f^{14}$	$6d^3$	$7s^2$		
108       Hassnium       Hs       [Rn] $5f^{14}$ $6d^6$ $7s^2$ 109       Meitnerium       Mt       [Rn] $5f^{14}$ $6d^7$ $7s^2$ 110       Darmstadtium       Ds       [Rn] $5f^{14}$ $6d^8$ $7s^2$ 111       Rontgenium       Rg       [Rn] $5f^{14}$ $6d^9$ $7s^2$	106	Seaborgium	Sg	[Rn] $5f^{14}$	$6d^4$	$7s^2$		
109 Meitnerium Mt [Rn] $5f^{14}$ $6d^7$ $7s^2$ 110 Darmstadtium Ds [Rn] $5f^{14}$ $6d^8$ $7s^2$ 111 Rontgenium Rg [Rn] $5f^{14}$ $6d^9$ $7s^2$	107	Bohrium	Bh	[Rn] $5f^{14}$	$6d^5$	$7s^2$		
109 Meitnerium Mt [Rn] $5f^{14}$ $6d^7$ $7s^2$ 110 Darmstadtium Ds [Rn] $5f^{14}$ $6d^8$ $7s^2$ 111 Rontgenium Rg [Rn] $5f^{14}$ $6d^9$ $7s^2$	108	Hassnium	Hs	[Rn] 5f <sup>14</sup>	$6d^6$	$7s^2$	•	
110 Darmstadtium Ds [Rn] $5f^{14}$ $6d^8$ $7s^2$ 111 Rontgenium Rg [Rn] $5f^{14}$ $6d^9$ $7s^2$	109	Meitnerium	Mt	[Rn] $5f^{14}$	$6d^7$			
111 Rontgenium Rg [Rn] $5f^{14}$ $6d^9$ $7s^2$	110	Darmstadtium	ı Ds	[Rn] $5f^{14}$	$6d^8$		-	
	111	Rontgenium	Rg	[Rn] $5f^{14}$	6d <sup>9</sup>	$7s^2$		
112 Ununbium Uub [Rn] $5f^{14}$ $6d^{10}$ $7s^2$	112	Ununbium	Uub	[Rn] $5f^{14}$	$6d^{10}$	$7s^2$		
113 Ununtrium Uut [Rn] $5f^{14}$ $6d^{10}$ $7s^2$ $7p^1$	113	Ununtrium	Uut	[Rn] $5f^{14}$	$6d^{10}$	$7s^2$	$7p^1$	
114 Ununquadium Uuq [Rn] $5f^{14}$ $6d^{10}$ $7s^2$ $7p^2$	114	Ununquadium	, -	[Rn] $5f^{14}$	$6d^{10}$		$7p^2$	
115 Ununpentium Uup [Rn] $5f^{14}$ $6d^{10}$ $7s^2$ $7p^3$	115	Ununpentium	Uup	[Rn] $5f^{14}$	$6d^{10}$		$7p^3$	
116 Ununhexium Uuh [Rn] $5f^{14}$ $6d^{10}$ $7s^2$ $7p^4$	116	Ununhexium		[Rn] $5f^{14}$	$6d^{10}$		$7p^4$	
118 Ununoctium Uuo [Rn] $5f^{14}$ $6d^{10}$ $7s^2$ $7p^6$	118	Ununoctium	Uuo	[Rn] 5f <sup>14</sup>	6d <sup>10</sup>	$7s^2$	$7p^6$	

# Classification of Elements on the Basis of Electronic Configurations

### 1. Bohr's Classification

The classification proposed by Bohr is based on complete and incomplete energy shells. The elements have been grouped into four types:

(i) Inert gases: In the atoms of these elements, the s-and p-subshells of the outermost shell are completely filled.

With the exception of helium which has  $1s^2$  configuration, all other have  $ns^2np^6$  configuration. Because of stable configuration, these elements do not show chemical activity under normal conditions. These are all gases under normal conditions and thus, termed as inert gases. Under special conditions, the higher members do form some compounds with other elements and hence, the name has been changed to **noble gases**. Seven elements He, Ne, Ar, Kr, Xe, Rn and Uuo belong to this group. This group was unknown at the time when Mendeleev presented the periodic table. These elements are the end members of the respective periods of the periodic table, respectively.

(ii) Representative or Normal elements: In these elements atoms have all shells complete except outermost shell which is incomplete. The number of electrons in the outermost shell varies from 1 to 7, i.e., the configuration of the outermost shell varies from  $ns^1$  to  $ns^2$   $np^5$ . These elements comprise of some metals, all non-metals and metalloids. These are the elements which are found in nature in abundance and active in nature. On account of this, these elements are called **representative elements**. All the three types of valencies are observed in the case of these elements. These elements have one of the following configurations in their outermost shell:

$$ns^{1}$$
,  $ns^{2}$ ,  $ns^{2} np^{1}$ ,  $ns^{2} np^{2}$ ,  $ns^{2} np^{3}$ ,  $ns^{2} np^{4}$ ,  $ns^{2} np^{5}$   
1 2 3 4 5 6 7

The number of electrons present in the outermost shell signify the group to which these elements belong.

(iii) Transition elements: In the atoms of these elements the outermost shell and the penultimate shell (next to the outermost) are incomplete. These elements have the general configuration  $(n-1)d^{1-9} ns^{0 \text{ or } 1 \text{ or } 2}$  either in the ground state or in excited state. These elements are present in fourth, fifth, sixth and seventh periods of periodic table and are called transition elements. The elements showing horizontal relationship as well as vertical relationship are termed transition elements. There are four transition series, every series consists of 9 elements each. Each series starts with a member of third group and ends with a member of first group.

```
1st series Sc 21 to Cu 29 3d^{1-9}4s^2

2nd series Y 39 to Ag 47 4d^{1-9}5s^2

3rd series La 57 to Au 79 5d^{1-9}6s^2

[The elements from Ce (58) to Lu (71) are not included]

4th series Ac 89, Rf (104), Db (105)

and 106 to 111 [The elements from Th (90) to Lr (103) are not included]
```

The elements belonging to this group are all metals.

- (iv) Inner-transition elements: Atoms of these elements have three outermost shells incomplete. The general configuration is  $(n-2)f^{1-14}(n-1)d^{0 \text{ or } 1} ns^2$ . There are two series of elements,
  - (a) Lanthanides or rare-earths from Ce (58) to Lu (71)
  - (b) Actinides from Th (90) to Lr (103).

Each series consists of 14 elements, *i.e.*, in the lanthanides, 4f is gradually filled up while in actinides, 5f is gradually filled up. The properties of these elements are similar to transition elements. The members of actinide series are radioactive and majority of them are not found in nature. The elements from atomic number 93 onwards are called transuranic elements and have been discovered by artificial means.

In this classification, the elements Zn, Cd and Hg have not been included in any of the four groups of elements. The elements Lu and Lr of the inner-transition group have (n-2)f shell complete consisting of 14 electrons, hence their inclusion in this group is not justified.

### 2. Differentiating Electron Classifications

(Division of elements into s-, p-, d-, f-Blocks)

This classification divides the elements into four types, *i.e.*, *s*-, *p*-, *d*- and *f*-block elements depending on the nature of the atomic shell into which the last electron enters. The last electron is called as **differentiating electron**. This classification is most rational and is now commonly in use. The energy shell into which the last electron enters is of highest energy. This may not always belong to the outermost energy shell. In general, it can be said that aufbau principle is followed in filling of various energy shells with few exceptions.

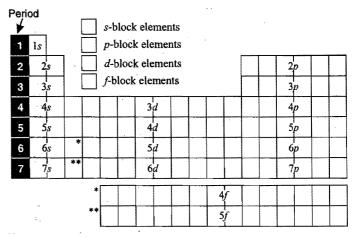


Fig. 1.4 Periodic table, illustrating division of elements into s-, p-, d-, f- Blocks

### ■ (i) s-Block Elements

In these elements, the last electron enters the ns energy shell. The maximum capacity of ns energy shell is of two electrons, thus, these elements have valency shell configuration either  $ns^1$  or  $ns^2$ .

The members of this block lie on the extreme left of the periodic table. The elements having  $ns^1$  configuration are called **alkali metals** (Group IA elements) while those having  $ns^2$  configuration are called **alkaline earth metals** (Group IIA elements). The elements of s-block are also called as **Reactive metals**.

# Periodic Table of the Elements (Long Form) (Representing Electron Configurations)

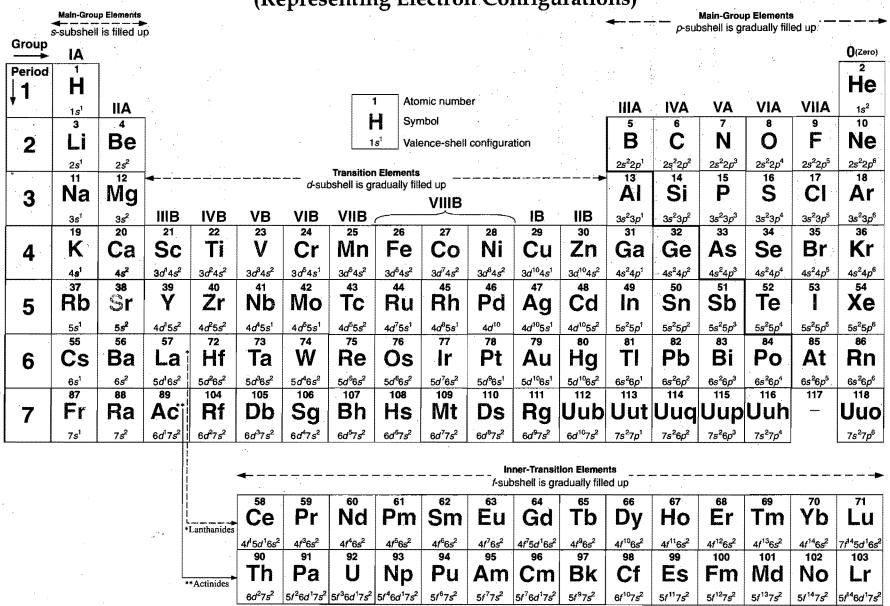


Fig. 1.5 A Modern Form of the Periodic Table (Long Form) (Representing valence-shell configurations of the elements)

$ns^1$	Elements	Group IA	Alkali	metals
H	1			1s1
Li	3	$1s^2$ , $2s^1$	or	[He] 2s <sup>1</sup>
Na			or	
K	19	2, 8, 8, 4s <sup>1</sup>	or	[Ar] 4s <sup>1</sup>
Rb	37	2, 8, 18, 8, 5s <sup>1</sup>	or	[Kr] 5s <sup>1</sup>
Cs	55	2, 8, 18, 18, 8, 6s <sup>1</sup>	or	[Xe] 6s <sup>1</sup>
Fr	87	2, 8, 18, 32, 18, 8, 7s <sup>1</sup>	or	[Rn] 7s <sup>1</sup>

# Group IIA

$ns^2$	Elements	Group IIA Alkaline	earth	metals
He	2	$1s^2$ (Actually belongs to zero group)	or	1s <sup>2</sup>
Be	4	$1s^2$ , $2s^2$	or	[He] 2s <sup>2</sup>
Mg	12	$1s^2$ , $2s^22p^6$ , $3s^2$	or	[Ne] 3s <sup>2</sup>
Ca	20	2, 8, 8, 4s <sup>2</sup>	or	[Ar] 4s <sup>2</sup>
Sr	38	2, 8, 18, 8, 5s <sup>2</sup>	or	[Kr] 5s <sup>2</sup>
Ва	56	2, 8, 18, 18, 8, 6s <sup>2</sup>	. or	[Xe] 6s <sup>2</sup>
Ra	88	2, 8, 18, 32, 18, 8, 7s <sup>2</sup>	or	[Rn] 7s <sup>2</sup>

#### General Characteristics of s-Block Elements:

The general characteristics of alkali metals (Li, Na, K, Rb, Cs and Fr) and alkaline earth metals (Be, Mg, Ca, Sr, Ba and Ra), i.e., s-block elements are the following:

- (i) They are soft metals, possess low melting and boiling points, have the largest atomic radii in their corresponding periods and are good conductors of heat and electricity.
- (ii) They have low values of ionisation energies and hence highly electropositive.
- (iii) They are very reactive and readily form ionic compounds. They show a fixed valency which depends on the number of electrons present in the outermost shell. The alkali metals show monovalency while alkaline earth metals show divalency. They are never found in free state in nature due to their reactive nature.
- (iv) On account of low ionisation energies and highly negative electrode potentials, they act as strong reducing agents. The alkali and alkaline earth metals cannot be prepared by doing electrolysis of aqueous solutions of their salts.
- (v) Except Be and Mg, they impart a characteristic colour to the flame.
- (vi) The compounds of s-block elements are predominently ionic and colourless. However, lithium and beryllium compounds are covalent in nature.
- (vii) They have great affinity for oxygen and nonmetals. The oxides are basic. The hydroxides are strong alkalies.
- (viii) They displace hydrogen from acids and form corresponding salts. "

(ix) With exception of Be and Mg, they decompose water and readily evolve hydrogen.

### (ii) p-Block Elements

In the atoms of these elements, the last electron enters the p-subshell of the outermost shell. In these elements npsubshell is gradually filled up. The valency shell configuration varies from  $ns^2 np^1$  to  $ns^2 np^6$ .

Order of the period	ns <sup>2</sup> np <sup>1</sup> (IIIrd group)	ns <sup>2</sup> np <sup>2</sup> (IVth) group)	ns <sup>2</sup> np <sup>3</sup> (Vth group)	ns <sup>2</sup> np <sup>4</sup> (VIth group)	ns <sup>2</sup> np <sup>5</sup> (VIIth group)	ns <sup>2</sup> np <sup>6</sup> (Zero group)
	Α	* <b>A</b>	·A	Α	A	
n = 2	В	С	N	0	F	Ne
	$2s^2 \ 2p^1$	$2s^2 2p^2$	$2s^2 2p^3$	$2s^2 2p^4$	$2s^2 \ 2p^5$	$2s^2 2p^6$
n = 3	Al		<b>P</b> ,	S		· .Ar
1.	$3s^2 \ 3p^1$		$3s^2 3p^3$	$3s^2 3p^4$	$3s^2 \ 3p^5$	$3s^2 3p^6$
n = 4	Ga	Ge	As	Se	Br	Kr
	$4s^2$ $4p^1$	$4s^2 4p^2$	$4s^2 4p^3$	$4s^2 4p^4$	$4s^2 4p^5$	$4s^2 4p^6$
n = 5	· In	Sn	Sb	Te	I	Xe
*	$5s^2 \ 5p^1$	$5s^2 5p^2$	$5s^2 5p^3$	$5s^2 5p^4$	$5s^2 5p^5$	$5s^2 5p^6$
n = 6	Tl	Pb	Bi	Po	At	Rn
	$6s^2 6p^1$	$6s^2 6p^2$	$6s^2 6p^3$	6s <sup>2</sup> 6p <sup>4</sup>	$6s^2 6p^5$	$6s^2$ $6p^6$
n = 7	Uut	Uuq	Uup	Uuh	· —.	Uuo
	$7s^2 7p^1$	$7s^2 7p^2$	$7s^2 7p^3$	$7s^2 7p^4$	€.	$7s^2 . 7p^6$
	Group 13	Group 14			Group 17	Group 18

These elements belong to subgroup A in the extended form of periodic table except zero group in which no subgroup is present.] These elements include some metals, all non-metals and metalloids. s-block and p-block elements are collectively called normal or representative elements (except zero group elements). Each period ends with a member of zero group (18th group), i.e., a noble gas with a closed shell ns<sup>2</sup>np<sup>6</sup> configuration. Prior to noble gas group, there are two chemically important groups of non-metals. These are halogens (group 17) and chalcogens (group 16).

### General Characteristics of p-Block Elements

- (i) *p*-block consists of the elements of six groups, *viz.*, IIIA, IVA, VA, VIA, VIIA and zero group. The number of electrons in the outermost shell varies from 3 to 8, i.e., they have general configuration,  $ns^2np^{1-6}$ . The number of electrons in the penultimate shell is either 2 or 8 or 18.
- (ii) Except F and inert gases, p-block elements show a number of oxidation states from +n to (n-8) where n is the number of electrons present in the outermost shell.

Group IIIA IVA VA VIA VIIA
Oxid. states +3 +4 to -4 +5 to -3 +6 to -2 +7 to -1

[Oxygen is an exception. However, it can show -2, -1,  $-1/2(KO_2)$ ,  $-1/3(KO_3)$  and  $+1/2(O_2PtF_6)$  oxidation states.]

- (iii) The *p*-block elements generally show covalency but higher members can show electrovalency. The highly electronegative elements like halogens, O, S, N, etc., show electrovalency by accepting electrons and forming anions. Some of the elements show coordinate valency also.
- (iv) In the period from left to right, there is regular increase in nonmetallic character. However, nonmetallic character decreases in the groups from top to bottom.
- (v) Ionisation energies increase from left to right in a period while decrease in a group from top to bottom. The members of V group and zero group have exceptionally high values of ionisation energies on account of half filled and fully filled orbitals in the valency shell.
- (vi) In every period, reducing nature decreases from left to right while oxidising nature increases. Reducing nature increases in a group from top to bottom. Halogens are strong oxidising agents.
- (vii) Most of them are highly electronegative. The electronegativity increases in a period from left to right and decreases in a group from top to bottom.
  - (viii) Most of them form acidic oxides.
- (ix) No member of *p*-block series or the salts imparts a characteristic colour to the flame.
- (x) Chemical properties change from group to group. It is difficult to summarise them.
- (xi) A number of elements of *p*-block series show the phenomenon of allotropy. Carbon, silicon, phosphorus, sulphur, boron, germanium, tin, arsenic, etc., show this property.
- (xii) Catenation property is shown by many elements of *p*-block series such as carbon, silicon, germanium, nitrogen, oxygen, sulphur, etc.

### **■ (iii)** d-Block Elements (Transition Elements)

The d-block elements are also called **transition metals**. In these elements, the last electron enters (n-1)d-subshell (d-orbitals of the penultimate orbit), i.e., (n-1) d-subshell is gradually filled up. The configuration varies from  $(n-1)d^1$   $ns^2$  to  $(n-1)d^{10}$   $ns^2$ . At certain places, the configurations are different than expected. The general configuration of these elements can be represented as  $(n-1)d^{1-10}$   $ns^0$  or 1 or 2. The elements of IIIB, IVB, VB, VIB, VIIB, VIII, IB and IIB belong to this block. These elements are also called **transition elements** as their properties are intermediate between s- and p-block elements. Transition elements must have incomplete penultimate d-subshell, either in the neutral atom or in any one of its stable oxidation states. All the transition elements are metals. These elements are classified into four series, i.e., 3d, 4d, 5d and 6d series corresponding to the filling of orbitals

of 3d, 4d, 5d and 6d subshells of third, fourth, fifth and sixth energy shells, respectively. Each series starts with a member of third group. Every series consists 10 elements each. The end members of 3d, 4d, 5d and 6d series are the members of second group. The expected configurations of these elements are tabulated in Fig. 1.6. The elements marked with asterisk (\*) have different actual configurations.

	3rd group	2nd group
3d series (1st transition series)	Sc (21) [Ar] 3d <sup>1</sup> 4s <sup>2</sup>	to Zn (30) [Ar] $3d^{10}4s^2$
4d series (2nd transition series)	Y (39) [Kr] $4d^15s^2$	to Cd (48) [Kr] 4d <sup>10</sup> 5s <sup>2</sup>
*5d series (3rd transition series)	La (57) [Xe] 5d <sup>1</sup> 6s <sup>2</sup>	to Hg (80) [Xe] $4f^{14}5d^{10}6s^2$
†6d series (4th transi- tion series)	Ac (89) [Rn] $6d^{1}7s^{2}$	to Unb (112) [Rn] 5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup>

<sup>\*</sup>The elements from Ce (58) to Lu (71) are not included.

#### General Characteristics of d-Block Elements

The general characteristics of *d*-block elements are :

- (i) They are all metals having high melting and boiling points. They are hard in nature and good conductors of heat and electricity. They are malleable, ductile and possess high tensile strength. They have high densities.
- (ii) The ionisation energies of most of *d*-block elements lie in between those of *s* and *p*-block elements. They are less electropositive than *s*-block elements and more electropositive than *p*-block elements. The members of 5*d* series such as Pt, Au, Hg, etc., are inert under ordinary conditions. They are called **noble metals**.
- (iii) *d*-block elements show variable valency. However, members of IIB group (Zn, Cd and Hg) do not show variable valency.
- (iv) Most of the compounds formed by *d*-block elements are coloured in the solid state or in solution.
- (v) Paramagnetism is common in d-block elements. This is due to the presence of unpaired electrons in (n-1)d orbitals.
- (vi) Most of the transition elements and their compounds act as good catalysts.
- (vii) They have high tendency to form complex compounds.
- (viii) They have high tendency to form alloys with other metals.
  - (ix) They form both ionic and covalent compounds.

### (iv) f-Block Elements (Inner-Transition Elements)

In these elements the last electron enters the (n-2)f energy shell [f-orbitals of the (n-2) main shell], i.e., (n-2)f subshell is gradually filled up. The configuration varies

<sup>†</sup>The elements from Th (90) to Lr (103) are not included.

	3 <i>d</i> -se	ries	Configuration	4d-ser	ies	Configuration	5 <i>d</i> -sei	ries	Configuration	6 <i>d-</i> ser	ies	Configuration
1.	Sc (21)		$[Ar] 3d^{1}4s^{2}$	Y (39)		[Kr] 4d <sup>1</sup> 5s <sup>2</sup>	La (57)		[Xe] $5d^{1}6s^{2}$	Ac (89)		[Rn] 6d <sup>1</sup> 7s <sup>2</sup>
2.	Ti (22)		$[Ar] 3d^24s^2$	Zr (40)		[Kr] $4d^25s^2$	Hf (72)		[Xe] $4f^{14}5d^26s^2$	Rf (104)		[Rn] $5f^{14}6d^27s^2$
3.	V (23)		$[Ar] 3d^34s^2$	*Nb (41)		[Kr] $4d^35s^2$	Ta (73)		[Xe] $4f^{14}5d^36s^2$	Db (105)		[Rn] 5f <sup>14</sup> 6d <sup>3</sup> 7s <sup>2</sup>
						or [Kr] 4d <sup>4</sup> 5s <sup>1</sup>						
4.	*Cr (24)		[Ar] 3d <sup>4</sup> 4s <sup>2</sup>	*Mo (42)		[Kr] 4d <sup>4</sup> 5s <sup>2</sup>	W (74)		[Xe] $4f^{14}5d^46s^2$	Unh (106)		[Rn] 5f <sup>14</sup> 6d <sup>4</sup> 7s <sup>2</sup>
			or [Ar] 3d <sup>5</sup> 4s <sup>1</sup>			or [Kr] 4d <sup>5</sup> 5s <sup>1</sup>				(Sg)		
5.	Mn (25)	d <sub>1</sub>	$[Ar] 3d^54s^2$	Tc (43)	dn 1	[Kr] $4d^55s^2$	Re (75)	dn 1	[Xe] $4f^{14}5d^56s^2$	Uns (107)	dn 1	[Rn] 5f <sup>14</sup> 6d <sup>5</sup> 7s <sup>2</sup>
		/ filled			, fillec	or [Kr] 4d <sup>6</sup> 5s <sup>1</sup>		/ filled up		(Bh)	/ filled up	
6.	Fe (26)	gradually	[Ar] $3d^64s^2$	*Ru(44)	lually	[Kr] $4d^65s^2$	Os (76)	gradually	[Xe] $4f^{14}5d^66s^2$	Uno (108)	gradually	[Rn] 5f <sup>14</sup> 6d <sup>6</sup> 7s <sup>2</sup>
		is grad			4d is gradually filled up	or [Kr] $4d^75s^1$		.22		(Hs)	is grac	
7.	Co (27)	3d	[Ar] $3d^7 4s^2$	*Rh (45)	4 <i>d</i>	[Kr] $4d^75s^2$	Ir (77)	5d	[Xe] 4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>	Une (109)	<i>p</i> 9	[Rn] 5f <sup>14</sup> 6d <sup>7</sup> 7s <sup>2</sup>
						or [Kr] $4d^85s^1$				(Mt)		
8.	Ni (28)		[Ar] $3d^84s^2$	*Pd (46)		[Kr] 4d <sup>8</sup> 5s <sup>2</sup>	*Pt (78)		[Xe] $4f^{14}5d^86s^2$	Uun (110)		[Rn] 5f <sup>14</sup> 6d <sup>8</sup> 7s <sup>2</sup>
						or [Kr] $4d^{10}5s^0$			[Xe] $4f^{14}5d^{9}6s^{1}$	(Ds)		;
9.	*Cu (29)	]	[Ar] $3d^94s^2$	*Ag (47)		[Kr] 4d <sup>9</sup> 5s <sup>2</sup>	*Au (79)		[Xe] $4f^{14}5d^{9}6s^{2}$	* Uuu (111)		[Rn] 5f <sup>14</sup> 6d <sup>9</sup> 7s <sup>2</sup>
			or [Ar] $3d^{10}4s^1$			or [Kr] $4d^{10}5s^1$	-		or [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>	(Rg)		or [Rn] 5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>1</sup>
10.	Zn (30)		[Ar] $3d^{10}4s^2$	Cd (48)		[Kr] 4d <sup>10</sup> 5s <sup>2</sup>	Hg (80)		[Xe] $4f^{14}5d^{10}6s^2$	Uub (112)		$[Rn]5f^{14}6d^{10}7s^2$

Fig. 1.6 d-block elements

from  $(n-2)f^1$   $(n-1)d^1$   $ns^2$  to  $(n-2)f^{14}$   $(n-1)d^1$   $ns^2$ . At some places the actual configurations are somewhat different than the expected configurations. Thus, the general configuration can be represented as  $(n-2)f^{0-14}$ ,  $(n-1)d^{0,1 \text{ or } 2}$   $ns^2$ . All f-block elements belong to 3rd group. The f-block elements are of two types:

- **(a) 4***f***-series** (Lanthanides): This series has 14 elements from Ce (58) to Lu (71). In these elements 4*f*-energy shell is gradually filled up.
- **(b)** *5f*-series (Actinides): This series also has 14 elements from Th (90) to Lr (103). In these elements *5f*-energy shell is gradually filled up. These elements are also called **inner transition elements**. All the elements are accommodated in 3rd group but separately written in two horizontal rows below periodic table.

4f-	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
elements	58	59	60	61	62	63	64	65	66	67	68	69	70	71
5 <i>f</i> -	Th	Pa	U	Np	Pu	Αm	Cm	Bk	Cf	Es	Fm	Md	No	Lr
elements	90	91	92	93	94	95	96	97	98	99	100	101	102	103

Note: Lanthanum ( $_{57}$ La) and actinium ( $_{89}$ Ac) are d-block elements. They are very similar in properties with lanthanides and actinides respectively and are usually studied along with them.

#### General Characteristics of f-Block Elements

The characteristics of *f*-block elements are similar to transition metals, *i.e.*, *d*-block elements. The important characteristics are given below:

- (i) All are metals.
- (ii) They show variable valency. +3 is the most important oxidation state. Few elements show +2 and +4 oxidation states.
  - (iii) They are paramagnetic in nature.
  - (iv) They form coloured compounds.
  - (v) They have tendency to form complexes.
- (vi) Chemically lanthanides are very similar. It is difficult to separate them from a mixture by application of a chemical property. The members of the actinide series are also similar in chemical properties.
- (vii) The members of actinide series are radioactive in nature. Elements above atomic number 92 are not found in nature. These are man-made elements. These are called transuranic elements.

# 1.7 EXTENDED OR LONG FORM OF PERIODIC TABLE

In order to remove the defects of Mendeleev's periodic table, a number of tables have been presented for the classification of elements. The best table out of these is the **extended** or **long form** of periodic table which has been shown in Fig. 1.7.

# Periodic Table of the Elements (Long Form)

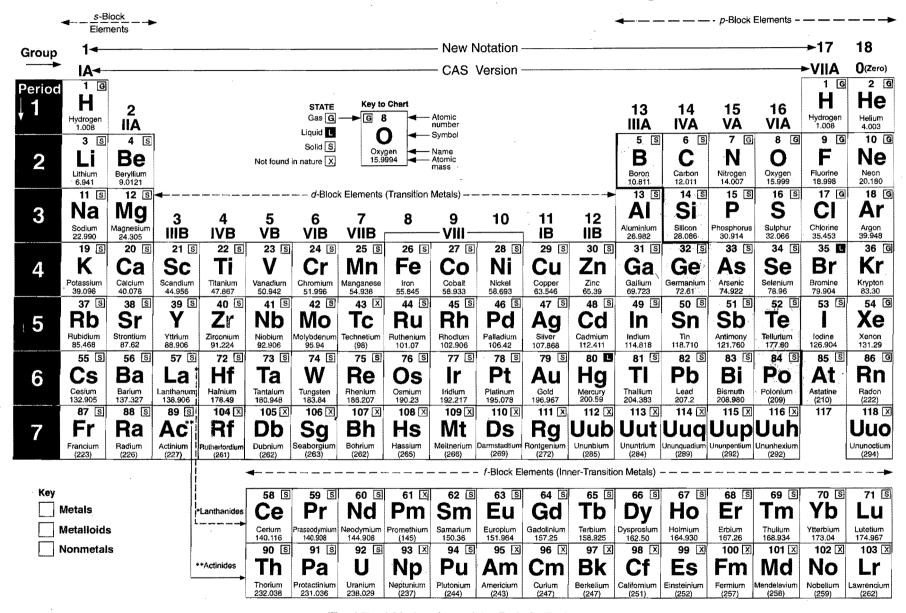


Fig. 1.7 A Modern form of the Periodic Table

the text (1) The new IUPAC format numbers the group from 1 to 18. The previous IUPAC numbering system and the system used by Chemical Abstracts Service (CAS) are also shown. For radioactive elements that do not occur in nature, the mass number of the most stable isotope is given in brackets with the longest half-life.

<sup>(2)</sup> The symbols for elements 104-111 used in this table are those proposed by the American Chemical Society and 112-118 proposed by IUPAC.

<sup>(3)</sup> There is no general agreement on the metalloids. Almost every list includes Si, Ge, As, Sb and Te but some also include B, At and Po in the list.

The credit for this table cannot be given to any single person but it incorporates the modifications suggested by many scientists, especially Rang, Werner, Bohr, Bury, etc. The table is most widely used these days and is also referred to as Bohr's table, since it follows the Bohr scheme of the arrangement of elements into four types based on electronic configuration of the elements. This table is just a graphical representation of the aufbau principle.

# ■ Structural Features of the Long Form of the Periodic Table

Like Mendeleev's periodic table, the long form of the periodic table consists of horizontal rows called **periods** and vertical columns called **groups**. These are described below:

#### **PERIODS:**

Periods are numbered as 1, 2, 3, 4, 5, 6, and 7 from top to bottom. The period number corresponds to the value of n, i.e., principal quantum number for the outermost or valence shell of the atoms of the elements belonging to that period. Number of elements in each period is twice of the atomic orbitals available in the energy level that are being filled.

**1st Period :** In the first period, the first main energy shell (K shell *i.e.*, n = 1) is filled. As it has only one orbital which can accommodate only two electrons, *i.e.*, only two elements are present. The first period consists of hydrogen (1s<sup>1</sup>) and helium (1s<sup>2</sup>).

**2nd Period**: In the second period, the second energy shell (*L*-shell *i.e.*, n=2) is completed. This energy shell has four orbitals, one 2s and three 2p orbitals, which can accommodate eight electrons and therefore, second period has eight elements from Li  $(2s^1)$  to Ne  $(2s^22p^6)$ .

**3rd period :** This period corresponds to the filling of third energy shell, *i.e.*, n = 3. There are nine orbitals, one 3s, three 3p and five 3d-orbitals in this shell. However, on the basis of aufbau principle, the 3d orbitals are higher in energy than 4s orbital. Thus, 3d orbitals are filled after filling of 4s orbital. Hence, only four orbitals, one 3s and three 3p orbitals are filled in this period. Consequently, this period, contains 8 elements from Na  $(3s^1)$  to Ar  $(3s^23p^6)$ .

**4th period:** The fourth period corresponds to the filling of fourth energy shell, *i.e.*, n = 4. Out of 4s, 4p, 4d and

4f-orbitals, the energies of 4d and 4f orbitals are higher than 5s orbital. Thus, 4s and 4p-orbitals are filled. However in between 4s and 4p-orbitals, five 3d-orbitals are also filled as their energies lie in between those orbitals. Hence, nine orbitals, one 4s, five 3d and three 4p-orbitals are filled. The fourth period contains 18 elements from potassium  $(4s^1)$  to krypton  $(3d^{10}4s^24p^6)$ . This period, therefore, includes first d-block series from scandium  $(Z=21, 3d^14s^2)$  to Zinc  $(Z=30, 3d^{10}4s^2)$ . Two s-block elements, ten d-block elements and six p-block elements are present.

**5th period**: Like fourth period, it also accommodates 18 elements as nine orbitals, one 5s, five 4d and three 5p orbitals are filled. It includes elements from rubidium  $(5s^1)$  to xenon  $(4d^{10}5s^25p^6)$ . This period, therefore, contains second d-block series from yttrium  $(Z=39, 4d^{10}5s^2)$  to cadmium  $(Z=48, 4d^{10}5s^2)$ . Two s-block, ten d-block and six p-block elements are present in this period.

**6th period**: The 6s, 4f, 5d and 6p-orbitals (i.e., sixteen orbitals) are filled accommodating 32 elements from caesium  $(6s^1)$  to radon  $(4f^{14}5d^{10}6s^26p^6)$ . This period includes third d-block series from lanthanum  $(Z=57,5d^16s^2$ —Here aufbau principle is violated) to mercury  $(4f^{14}5d^{10}6s^2)$ . The filling of 4f-orbitals begins from cerium  $(Z=58,4f^15d^16s^2)$  and ends up at lutetium  $(Z=71,4f^{14}5d^16s^2)$ . These fourteen elements constitute 4f-series (Lanthanides). As the period can accommodate to the maximum of 18 elements, these 14 elements of 4f-series are separately placed in a horizontal row below the periodic table.

**7th period :** Like sixth period, seventh period is also expected to accommodate 32 elements corresponding to filling of sixteen orbitals, *i.e.*, one 7s, seven 5f, five 6d and three 7p orbitals. However, at present this period is incomplete consisting 31 elements. One element of p-block bearing atomic numbers 117 is to be discovered to complete this period. The period includes two s-block elements, 10d-block elements, 14f-block elements and five p-block elements at present. 14 members of 5f-series (actinides) are also separately accommodated in a horizontal row below the periodic table like 4f-series.

The number of elements and the corresponding orbitals being filled are given in the following table:

Period	Energy level being filled	Orbitals being filled	First member	Last member		Total number of electrons or elements in the period		
1	n = 1	1 <i>s</i>	H(Z=1)	He $(Z=2)$	2	= 2		
2	n = 2	2s 2p	Li $(Z = 3)$	Ne $(Z = 10)$	2 + 6	= 8		
3	n = 3	3s 3p	Na $(Z = 11)$	Ar  (Z = 18)	2 + 6	= 8		
4	n=4	<b>4</b> s 3d <b>4</b> p	K (Z = 19)	Kr (Z = 36)	2 + 10 + 6	= 18		
5	n = 5	5s <b>4</b> d 5p	Rb $(Z = 37)$	Xe   (Z = 54)	2 + 10 + 6	= 18		
6	n = 6	6s 4f 5d 6p	Cs (Z = 55)	Rn $(Z = 86)$	2 + 14 + 10 + 6	= 32		
7	n = 7	7s 5f 6d 7p	Fr (Z = 87)	Uuo $(Z = 118)^*$	2 + 14 + 10 + 6	= 32*		

They are *p*-block elements and their number is quite low. Six of the nonmetals carbon, boron, phosphorus, sulphur, selenium and iodine are solids. Bromine is the only liquid nonmetal at room temperature. The remaining nonmetals—nitrogen, oxygen, fluorine, chlorine, hydrogen and noble gases are gases. Nonmetals are generally (i) brittle (ii) nonlustrous (iii) have low melting and boiling points (carbon and boron are exceptions) (iv) nonconductors of heat (v) capable of forming acidic oxides (vi) do not evolve hydrogen from acids.

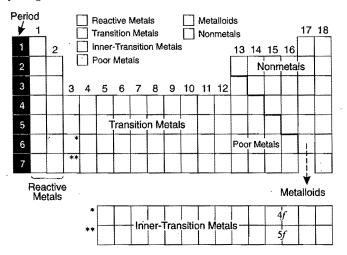


Fig. 1.10 Blocks of elements representing similar properties in the periodic table

#### Metalloids:

There are some elements which do not fit completely into either metal or nonmetal class. Elements which have mixed properties of metals and nonmetals both are called semimetals or metalloids. Silicon, germanium, arsenic, antimony and tellurium are metalloids. But some scientists include boron, polonium and astatine also in the list of metalloids.

In most respects, metalloids behave as non-metals, both chemically and physically. However, in their most important physical property, the electrical conductivity, they somewhat resemble metals. Metalloids tend to be **semiconductors**; they conduct electricity, but not nearly so well as metals. This property, particularly found in silicon and germanium, is responsible for the remarkable progress made during the last fifty years in the field of solid-state electronics. The operations of every computer, audio system, TV receiver, DVD or CD player relies on transistors made from semiconductors.

In periodic table, the metallic character increases from top to bottom in a group while metallic character decreases from left to right along a period.

### Superiority of the Long Form of the Table over Mendeleev's Periodic Table

- (i) This table is based on a more fundamental property, *i.e.*, atomic number.
- (ii) It correlates the position of the element with its electronic configuration more clearly.

- (iii) The completion of each period is more logical. In a period as the atomic number increases, the energy shells are gradually filled up until an inert gas configuration is reached. It eliminates the even and odd series of IV, V and VI periods of Mendeleev's periodic table.
- (iv) The position of VIII group is appropriate in this table. All the transition elements have been brought in the middle as the properties of transition elements are intermediate between *s* and *p*-block elements.
- **(v)** Due to separation of two subgroups, dissimilar elements do not fall together. One vertical column accommodates elements with same electronic configuration thereby showing same properties.
- (vi) In this table a complete separation between metals and nonmetals has been achieved. The nonmetals are present in upper right corner of the periodic table.
- (vii) There is a gradual change in properties of the elements with increase in their atomic numbers, *i.e.*, periodicity of properties can be easily visualised. The same properties of recurrence in properties occur after the intervals of 2, 8, 8, 18, 18 and 32 elements which indicates the capacity of various periods of the table.
- (viii) This arrangement of elements is easy to remember and reproduce.

### Defects of Long Form of Periodic Table

The long form of periodic table has following defects:

- **(i) Position of hydrogen:** The position of hydrogen is not fixed in this table also. It is placed either in IA or in VIIA group.
- (ii) Position of lanthanides and actinides: No individual places have been assigned to these 28 elements in the periodic table.
- (iii) This table does not reflect the exact distribution of electrons among all the orbitals of the atoms of all the elements.

# 1.8 POSITION OF AN ELEMENT ON THE BASIS OF ELECTRONIC CONFIGURATION

The block, period and group of an element can be easily decided from its electronic configuration of the element (Fig. 1.4).

- (i) The block of the element is decided on the basis of the type of the orbital on which the last electron is accommodated. If the last electron enters into s-subshell or *p*-subshell or *d*-subshell or *f*-subshell, then the element belongs to s-block or *p*-block or *d*-block or *f*-block respectively.
- (ii) The period to which an element belongs depends on the total number of orbits (shells) on which electrons are present.

or

The serial number of the period corresponds to the principal quantum number (p.q.no.) of the outermost shell on which the electrons are present.

C1	17	2, 8, 7	[Ne] $3s^23p^5$	belongs to
		Three orbits	p.q.no. 3	3rd period
Pb	82	2, 8, 18, 32, 18, 4,	[Xe] $4f^{14}5d^{10}6s^26p^2$	belongs to
		Six orbits	p.q.no. 6	6th period

- (iii) To decide about the group number (IUPAC), the number of electrons present on the outermost shell or / and penultimate shell [next to the outermost, *i.e.*, (n-1) shell] are counted.
- (a) If the last orbit contains 1 or 2 electrons, the group number is 1 or 2 respectively (Helium is an exception which belongs to group 18). There should not be any d-orbital in the penultimate shell, *i.e.*, in the penultimate shell either 2 electrons  $[(n-1)s^2]$  or 8 electrons  $[(n-1)s^2p^6]$  electrons are present.

ns <sup>1</sup>	→ 1st group	• :	$ns^2 \longrightarrow 2nd grou$	Р
K	19	2, 8, 8, 1	[Ar] 4s <sup>1</sup>	Group 1
Sr	38	2, 8, 18, 8, 2	[Kr] 5s <sup>2</sup>	Group 2
Be	4	2, 2	[He] 2s <sup>2</sup>	Group 2
Li	3	2, 1	[He] 2s <sup>1</sup>	Group 1

(b) If the last orbit has 3 or more electrons, then the group number is the sum of electrons in the last orbit plus 10. Such an element belongs to *p*-block.

s	16	2, 8, 6	[Ne]	$3s^23p^4$	6 + 10 = 16
Ge	32	2, 8, 18, 4	[Ar]	$3d^{10}4s^24p^2$	<i>i.e.</i> , 16th group $4 + 10 = 14$
Xe	54	2, 8, 18, 18, 8	[Kr]	$4d^{10}5s^25p^6$	<i>i.e.</i> , 14th group $10 + 8 = 18$
Αt	85	2, 8, 18, 32, 18, 7	[Xe]	$4f^{14}5d^{10}6s^26p^5$	<i>i.e.</i> , 18th group $10 + 7 = 17$
					i.e., 17th group

(c) If the last orbit contains 1 or 2 electrons and (n-1)d-orbitals where electrons are present, then group number is equal to the sum of electrons in the last orbit and (n-1)d-orbitals. Such an element belongs to d-block.

Cr 24	2, 8, 8 + 5, 1	[Ar] 3d <sup>5</sup>	$4s^1   5+1=6$
Cu 29	2, 8, 8 + 10, 1	[Ar] 3d <sup>1</sup>	i.e., 6th group $10 + 1 = 11$
			i.e., 11th group
Ku 44	2, 8, 18, 8 + 7, 1	[Kr] 4d <sup>7</sup>	7 + 1 = 8 <i>i.e.</i> , 8th group
Hf 72	2, 8, 18, 32, 8 + <b>2</b> , <b>2</b>	[Xe] 4f <sup>14</sup>	
			i.e., 4th group

# 1.9 ATOMIC PROPERTIES OR PERIODIC PROPERTIES OF ELEMENTS

The physical properties of the elements can be divided into two categories :

(i) Properties of individual atoms: Properties such as atomic and ionic radii, ionisation enthalpy, electron gain

enthalpy, valency, screening effect, effective nuclear charge and electronegativity are the properties of individual atoms and directly dependent on their electronic configurations.

(ii) Properties of group of atoms: Properties such as melting point, boiling point, heat of fusion, heat of vaporization, density, atomic volume, etc., are the properties of group of atoms together and are indirectly related to their electronic configurations.

All these properties which are directly or indirectly dependent on the electronic configuration of the elements are called atomic properties.

Since electronic configurations of the elements are periodic function of atomic numbers of the elements, therefore, these atomic properties are also a periodic function of atomic numbers of the elements. On account of this, atomic properties are also called **periodic properties**.

### Periodicity in Properties

The rigid meaning of the word periodic is that a particular property is repeated in a system at regular intervals. The term periodicity in properties in the classification of elements means that same properties of the elements reappear at definite intervals when the elements are arranged in the order of their increasing atomic numbers. In modern periodic table, these intervals are 2, 8, 8, 18, 18 and 32, *i.e.*, similar properties are observed with elements belonging to the same subgroup which have been arranged in subgroups after the difference of either 2 or 8 or 18 or 32 in atomic numbers as similar valency-shell electronic configurations recur after certain regular intervals of atomic number. This is the cause of periodicity in properties.

The real meaning of the word periodic in any classification of elements is that when the elements are arranged in order of their increasing atomic numbers in the same period or a group, there is gradual change (*i.e.*, increase or decrease) in a particular property. In a period, the gradual change is due to the gradual change of electronic configuration from member to member. Some of the properties which depend on electronic configuration of elements such as screening effect, effective atomic number, atomic radii, ionic radii, ionisation potential, electron affinity, electronegativity, etc., follow the general trend of periodicity.

In a group, the chemical properties of the elements remain nearly the same due to same valence shell configuration. There is gradual change in physical properties due to gradual change in the size of atoms due to start of new energy shell.

We shall discuss now the periodicity or periodic trends in some of the properties such as screening effect, effective nuclear charge, atomic and ionic radii, ionisation enthalpy, electron gain enthalpy, electronegativity, etc. We shall restrict our study especially in the case of *s*- and *p*-block (*i.e.*, normal or representative) elements.

# 1.10 THE SCREENING EFFECT OR SHIELDING EFFECT

In a multielectron atom, the electrons of the valency shell (outermost shell) are attracted towards the nucleus and also these electrons are repelled by the electrons present in the inner shells. On account of this, the actual force of attraction between the nucleus and the valency electrons is somewhat decreased by the repulsive forces acting in opposite direction. This decrease in the force of attraction exerted by the nucleus on the valency electrons due to the presence of electrons in the inner shells, is called screening effect or shielding effect. The magnitude of the screening effect depends upon the number of inner electrons, i.e., higher the number of inner electrons, greater shall be the value of screening effect. The screening effect constant is represented by the symbol  $\sigma$ . The magnitude of ' $\sigma$ ' is determined by the Slater's rules. The contribution of inner electrons to the magnitude of  $'\sigma'$  is calculated in the following ways:

### For *ns* or *np* Orbital Electrons

- (i) Write the electronic configuration of the element in the following order and group them as,
- (1s), (2s 2p), (3s 3p), (3d), (4s 4p), (4d 4f), (5s 5p), (5d 5f), (6s 6p), etc.
- (ii) Electrons to the right of the (ns, np) group are not effective in shielding the ns or np electrons and contribute nothing to  $\sigma$ .
- (iii) All other electrons in the (*ns*, *np*) group contribute to the extent of 0.35 each to the screening constant (except for 1s for which the value is 0.30).
- (iv) All the electrons in the (n-1)th shell contribute 0.85 each to the screening constant.
- (v) All the electrons in the (n-2)th shell or lower contribute 1.0 each to the screening constant.

#### For d- or f-electrons

Rules (i) to (iii) remain the same but rules (iv) and (v) get replaced by the rule (vi).

(vi) All the electrons in the groups lying left to (nd, nf) group contribute 1.0 each to the screening effect.

**Example 1.** Calculation of screening constants of alkali metals for valency electrons.

Li 2, 
$$1 = 2 \times 0.85$$
 = 1.7  
Na 2,  $8$ ,  $1 = 8 \times 0.85 + 2 \times 1$  = 8.8  
K 2,  $8$ ,  $8$ ,  $1 = 8 \times 0.85 + 10 \times 1$  = 16.8  
Rb 2,  $8$ ,  $18$ ,  $8$ ,  $1 = 8 \times 0.85 + 28 \times 1$  = 34.8  
Cs 2,  $8$ ,  $18$ 

**Example 2.** Calculation of screening constants of members of second period for valency electrons.

Li 
$$2, 1 = 2 \times 0.85 = 1.7$$
  
Be  $2, 2 = 0.35 + 2 \times 0.85 = 2.05$ 

B 2, 
$$3 = 2 \times 0.35 + 2 \times 0.85 = 2.40$$
  
C 2,  $4 = 3 \times 0.35 + 2 \times 0.85 = 2.75$   
N 2,  $5 = 4 \times 0.35 + 2 \times 0.85 = 3.10$   
O 2,  $6 = 5 \times 0.35 + 2 \times 0.85 = 3.45$   
F 2,  $7 = 6 \times 0.35 + 2 \times 0.85 = 3.80$   
Ne 2,  $8 = 7 \times 0.35 + 2 \times 0.85 = 4.15$ 

**Example 3.** Calculation of screening constants in zinc (a) for a 4s-electron (b) for a 3d-electron.

- (a) The electronic configuration of zinc (30) is,  $(1s)^2 (2s 2p)^8 (3s 3p)^8 (3d)^{10} (4s)^2$  $\sigma = 10 \times 1.0 + 18 \times 0.85 + 1 \times 0.35 = 25.65$
- (b) For 3*d*-electron,

$$\sigma = 18 \times 1.0 + 9 \times 0.35 = 21.15$$

It is clear from the examples (1) and (2) that the magnitude of screening constant in the case of s- and p-block elements increases in a period as well as in a group as the atomic number increases.

From the example (3), it is evident that the electrons in different orbitals are differently affected by the same nuclear charge depending upon their proximity to the nucleus.

### 1.11 EFFECTIVE NUCLEAR CHARGE

Due to screening effect the valency electron experiences less attraction towards nucleus. This brings decrease in the nuclear charge (Z) actually present on the nucleus. The reduced nuclear charge is termed **effective nuclear charge** and is represented by  $Z^*$ . It is related to actual nuclear charge (Z) by the following formula:

$$Z^* = (Z - \sigma)$$
, where  $\sigma$  is screening constant.

It is observed that magnitude of effective nuclear charge increases in a period when we move from left to right.

II period	Li	Be	В	C	N	О	F	Ne
Z	3	4	. 5	6	7	8	9	10
σ								
$Z^* = (Z - \sigma)$	1.3	1.95	2.60	3.25	3.90	4.55	5.20	5.85

In a subgroup of normal elements the magnitude of effective nuclear charge remains almost the same.

Alkali group	Li	Na	K	Rb	Cs
$Z^{\tau}$	3	11	19	37	55
σ	1.7	8.8	16.8	34.8	52.8
$Z^* = (Z - \sigma)$	1.3	2.2	2.2	2.2	2.2
IIA group	Be	Mg	Ca	Sr	Ba
Z	4	- 12	20	38	- 56
σ	2.05	9.15	17.15	35.15	53.15
$Z^* = (Z - \sigma)$	1.95	2.85	2.85	2.85	2.85

### 1.12 ATOMIC RADIUS

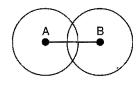
An atom is assumed to be spherical in shape and, thus, the size of atom is generally given in terms of radius of the sphere and is called atomic radius. It is usually defined as the distance between the centre of the nucleus and outermost shell where electron or electrons are present. The exact measure of atomic radius is not easy due to following reasons:

- (i) The atom does not have well defined boundary. The probability of finding the electron is never zero even at large distances from the nucleus.
- (ii) It is not possible to get an isolated atom. The electron density around an atom is affected by the presence of neighbouring atoms, *i.e.*, the size of the atom changes in going from one set of environment to another.
- (iii) The size of an atom is very small, of the order of about  $1.2\text{\AA}$ , i.e.,  $1.2 \times 10^{-10}$  m.

An estimate of the size of the atom can, however, be made by knowing the distance between the atoms in the combined state. The distance between the atoms, *i.e.*, bond lengths are generally measured by the application of techniques such as X-ray diffraction, electron diffraction, infrared spectroscopy, nuclear magnetic resonance spectroscopy, etc. However, bond lengths change with different type of bonding. Three types of radius are commonly used, *i.e.*, (a) covalent radius (b) crystal radius (c) van der Waals' radius.

(a) Covalent radius: Covalent radius is defined as half of the distance between two nuclei of two like atoms

bonded together by a single covalent bond. Consider a homonuclear diatomic molecule  $A_2$ , bonded together by single covalent bond. It is assumed that electron clouds of each atom touch each other. Let the bond length be  $d_{A-A}$ . Then  $d_{A-A} = r_A + r_A = 2r_A$ .



So 
$$r_A = \frac{d_{A-A}}{2}$$

In a hetero-nuclear diatomic AB molecule if both atoms are linked by a single covalent bond and have nearly same electronegativity, the bond length  $d_{A-B}$  is equal to sum of covalent radius of the two atoms.

$$d_{A - B} = r_A + r_B$$

Knowing the bond length and covalent radius of one of the atoms, the radius of the other atom can be determined. Covalent radius is used for non-metals.

[When there is large difference in the electronegativity of two elements A and B, the bond between A and B will have somewhat ionic character and the bond length  $d_{A op B}$  will be shorter than expected. In such cases, the following relationship should be used :

$$d_{A-B} = r_A + r_B - 0.09(X_A - X_B)$$

 $X_A$  and  $X_B$  are the electronegativities of elements A and B.

For example,

- (a) Bond length ( $d_{H-H}$ ) in hydrogen molecule is 0.74Å.
- ∴ Covalent radius of hydrogen =  $\frac{d_{H-H}}{2} = \frac{0.74}{2} = 0.37 \text{ Å}$
- (b) Bond length ( $d_{Cl-Cl}$ ) in chlorine molecule is 1.98Å.

∴ Covalent radius of chlorine = 
$$\frac{d_{\text{Cl--Cl}}}{2} = \frac{1.98}{2} = 0.99 \text{ Å}$$

(c) Bond length  $(d_{C-C})$  in diamond is 1.54Å.

$$\therefore$$
 Covalent radius of carbon =  $\frac{d_{C-C}}{2} = \frac{1.54}{2} = 0.77 \text{ Å}$ 

(d) Bond length ( $d_{Si-C}$ ) in carborundum is 1.93Å.

$$d_{\text{Si}-C} = r_{\text{Si}} + r_{\text{C}}$$
  
or  $1.93 = r_{\text{Si}} + 0.77$  (:  $r_{\text{C}} = 0.77\text{Å}$ )  
or  $r_{\text{Si}} = 1.93 - 0.77 = 1.16\text{Å}$ 

(e) Bond length  $(d_{C-C_1})$  in CCl<sub>4</sub> is 1.76Å.

.. 
$$d_{C-Cl} = r_C + r_{Cl}$$
  
or  $1.76 = r_C + 0.99$  (·  $r_{Cl} = 0.99\text{Å}$ )  
or  $r_C = 1.76 - 0.99 = 0.77\text{Å}$ 

**Note:** Elements may have multiple bonds in compounds which are always shorter than single bonds.

$$C \longrightarrow C$$
,  $C \Longrightarrow C$   
1.54Å 1.33Å 1.20Å

The double and triple bond radii are calculated in the similar fashion as single covalent radius.

Double bond radius of carbon = 1.33/2 = 0.665Å

Triple bond radius of carbon = 1.20/2 = 0.60Å

The double and triple bond radii of an atom are approximately 0.87 and 0.78 times the single bond radius respectively.

(b) Crystal Radius: It is used for metal atoms which are assumed to be closely packed spheres in the metallic crystal, i.e., atoms are supposed to touch one another: It is defined as one half the distance between the nuclei of two adjacent metal atoms in the metallic closed packed crystal lattice in which the metal exhibits a coordination number of 12. It is also called metallic radius.

For example, the distance between the two adjacent potassium atoms in solid potassium is 4.62Å. Therefore, the metallic radius of potassium is 4.62/2 = 2.31 Å.

A metallic radius is always longer than covalent radius.

Metal	Covalent radius (Å)	Crystal radius (Å		
Sodium	1.54	1.86		
Potassium	2.03	2.31		
Copper	1.17	1.28		
Barium	1.98	2.22		
Aluminium	1.20	1.43		

Atomic radius is expressed either in nanometre (1 nm =  $10^{-9}$  m) or in angstrom (1 Å =  $10^{-10}$  m) or in picometre (1 pm =  $10^{-12}$  m).

(c) van der Waals' radius: It is half of the distance between the nuclei of two non-bonded neighbouring atoms of two adjacent molecules in solid state.

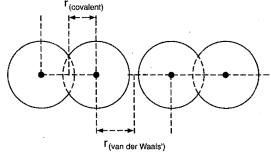


Fig. 1.12 Comparison of covalent and van der Waals' radius

The magnitude of the van der Waals' radius depends upon the packing of molecules of the element in solid state. For example, the distance between adjacent chlorine atoms of the two neighbouring molecules in solid state is 3.6Å. Therefore, the van der Waals' radius of chlorine is 3.6/2 = 1.8 Å.

van der Waals' radius of an element is always larger than its covalent radius.

A comparison of three types of radius shows that covalent radius of an atom is shortest while van der Waals' radius is the longest.

van der Waals' radius > Crystal radius > Covalent radius van der Waals' forces are weak, thus the distances between the atoms held by these forces are much larger than held by covalent bonding. A covalent bond is formed by overlap of two half filled atomic orbitals, thus a part of the electron cloud becomes common between two atoms. Due to these reasons van der Waals' radius is always higher than covalent radius. In case of a crystal, the valence electrons of the atoms are mobile, therefore, they are only weakly attracted. The metallic forces are thus weaker than covalent forces. On account of this, crystal (metallic) radius is larger than covalent radius.

[van der Waals' forces < Metallic forces < Covalent forces]

Note: For simplicity, we may use the term atomic radius for both covalent or crystal (metallic) radius depending on whether the element is a non-metal or a metal. However, the atomic radii of inert gases are usually expressed in terms of van der Waals' radii as they do not form chemical compounds.

#### Variation of Atomic Radii

(a) Variation in a Period: As we move from left to right across a period, there is regular decrease in atomic radii of the representative elements. This is due to the fact that number of energy shells remain the same in a period but nuclear charge increases gradually as the atomic number increases. This increases the force of attraction towards nucleus which brings contraction in size. This can also be explained on the basis of effective nuclear charge which increases gradually in a period, *i.e.*, electron cloud is attracted more strongly towards nucleus as the effective nuclear charge becomes more and more as we move in a period. The increased force of attraction brings contraction in size.

Atomic radius 
$$\propto \frac{1}{Z_{\text{eff.}}}$$
  $(Z_{\text{eff.}} = Z - \sigma)$ 

 $Z_{eff.}$  = Effective nuclear charge; Z = Atomic number;  $\sigma$  = Shielding effect

2nd period Li Be B C N O F 
$$Z_{\rm eff.}=(Z-\sigma)$$
 (3-1.7) (4-2.05) (5-2.40) (6-2.75) (7-3.10) (8-3.45) (9-3.80) = 1.3 = 1.95 = 2.60 = 3.25 = 3.90 4.55 = 5.20 Atomic 1.23 0.89 0.80 0.77 0.75 0.73 0.72 radius (Å)

**(b)** Variation in a Group: Atomic radii in a group increase as the atomic number increases. The increase in size is due to extra energy shells which outweigh the effect of increased nuclear charge. The following table illustrates

the periodicity in atomic radii (covalent radii) of representative elements. The radii are in angstroms.

Period/Group→	I	. II	III	IV	V	VI	VII	
↓ 1	H 0.37							
2	Li	Be	В	С	N	О	F	
•	1.23	0.89	0.80	0.77	0.75	0.73	0.72	
3	Na	Mg	Al	Si	P	S	Cl	ses
	1.54	1.36	1.20	1.17	1.10	1.04	0.99	Increases
4	K	Ca	Ga	Ge	As	Se	Br	Ĕ
	2.03	1.74	1.26	1.22	1.20	1.16	1.14	Į.
5	Rb	Sr	In	Sn	Sb	Te	I	
	2.16	1.91	1.44	1.41	1.40	1.36	1.33	
6	Cs	Ва	Tl	Pb	Bi	Po		ĺ
	2.35	1.98	1.48	1.47	1.46	1.46		
<del>3112</del>			Decrea	ses		,	•	•

The atoms of zero group elements do not form chemical bonds. Hence, their van der Waals' radii are considered which are always larger than covalent radii of halogens.

The decrease in the size of transition elements is small since the differentiating electrons enter into inner 'd' levels. The additional electrons into (n-1)d levels effectively screen much of increased nuclear charge on the outer ns electrons and therefore, size remains almost constant.

However, in vertical columns of transition elements, there is an increase in size from first member to second member as expected but from second member to third member, there is

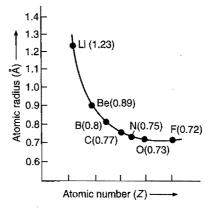


Fig. 1.13 Variation of atomic radii (covalent) in a period

very small change in size and sometimes sizes are same. This is due to **Lanthanide contraction** (in the lanthanide elements

differentiating electrons enter into 4*f* levels. Since these electrons do not effectively screen the valency electrons from the increased nuclear charge, the size gradually decreases. This decrease is termed lanthanide contraction).

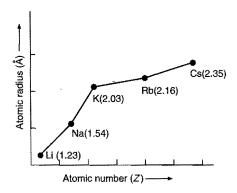


Fig. 1.14 Variation of atomic radius (covalent) down a group

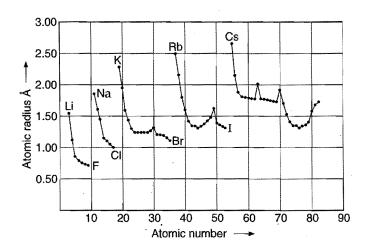


Fig. 1.15 Variation in atomic radii in periods (Metallic radii for metals and covalent radii for non-metals)

Element	Ce	Pr	Nd	Pm	Sm		Tb	 Lu
Atomic radius Å	1.65	1.65	1.64	1.63	1.62	•	1.59	1.56
(Covalent)								

The increase in size that arises due to period change in second and third transition series is almost compensated by the lanthanide contraction.

1st Tr. series	Sc	Ti	V	Cr .	 Cu
At. radius Å (Covalent)	1.44	1.32	1.22	1.17	1.17
2nd Tr. series	Y	Zr	Nb	Mo	 Ag
At. radius Å (Covalent)	1.62	1.45	1.34	1.29	1.34
3rd Tr. series	La	Hf	Ta	· W	 Au
At. radius Å (Covalent)	1.69	1.45	1.34	1.30	1.34

The following table illustrates the metallic radii (Crystal radii) in angstroms:

L1	Вe														
1.52	1.12														
Na	Mg				*		•					Al	Si	P	
1.86	1.60											1.43	1.32	1.28	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	
2.31	1.97	1.64	1.47	1.35	1.29	1.37	1.26	1.25	1.25	1.28	1.37	1.23	1.37	1.39	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn .	Sb	
2.48	2.15	1.82	1.60	1.47	1.40	1.35	1.34	1.34	1.37	1.44	1.52	1.67	1.62	1.59	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	
2.65	2.22	1.87	1.59	1.47	1.41	1.37	1.35	1.36	1.39	1.44	1.57	1.70	1.75	1.70	

### **Conclusions**

- (i) The alkali metals which are present at the extreme left of the periodic table have the largest size in a period.
- (ii) The halogens which are present at the extreme right of the periodic table have the smallest size.
- (iii) The sizes of the atoms of inert gases are, however, larger than those of preceding halogens because in inert gases van der Waals' radii are taken into consideration.
- (iv) In transition series, the decrease in size is small as the additional electrons in (n-1)d levels effectively screen much of the nuclear charge on the ns electrons.
- (v) In 4f-series, there is continuous decrease in size with increase in atomic number. This decrease is termed Lanthanide contraction.
- (vi) In a group of normal elements, there is continuous increase in size with increase in atomic number.
- (vii) In a group of transition elements, there is an increase in size from first member to second member as expected but from second member to third member, there is very small change in size and sometimes sizes are same. This is due to Lanthanide contraction.

### 1.13 IONIC RADIUS

Ionic radii are related to the ions present in ionic (crystalline) solids. Ions are formed when neutral atoms lose one or more electrons or gain one or more electrons. A positive ion results when a neutral atom loses one or more electrons. A positive ion is called **cation**. A negative ion is formed when a neutral atom gains one or more electrons. The negative ion is termed anion. The effective size of these ions is termed ionic radius. It is defined as the distance between the nucleus and outermost shell of an ion or it is the distance between the nucleus and the point where the nucleus exerts its influence on the electron cloud.

Like atomic radii, the accurate measurement of ionic radii is also not easy. However, the internuclear distance between two oppositely charged ions in a crystal can be taken as the sum of the radius of cation and radius of the anion by assuming spherical shapes of the ions and both are touching each other. X-ray technique is used to measure the internuclear distances. Knowing the radius of one ion, the radius of the other ion can be calculated.

For example, in NaCl crystal, the internuclear distance of two ions is 2.76Å. The radius of Na $^+$  ion is 0.95Å (Pauling theoretical method). Therefore, the radius of Cl $^-$  ion is 2.76 – 0.95 = 1.81Å.

### Comparison of the Ionic Radii with Corresponding Atomic Radii

- (a) The radius of the cation is always smaller than the atomic radius of its parent atom. This is due to the fact that nuclear charge in the case of a cation is acting on a lesser number of electrons and pulls them closer, *i.e.*, effective nuclear charge of a cation is always greater than the neutral atom and thus, electron cloud contracts.
- **(b)** The radius of the anion is always larger than the atomic radius of its parent atom. In an anion as electron or electrons are added to the neutral atom, the nuclear charge acts on more electrons so that each electron is held less tightly and thereby the electron cloud expands, *i.e.*, effective nuclear charge of an anion is always smaller than the neutral atom and thus, electron cloud expands.

**Comparative Sizes of Atoms and their Cations** 

Atom	Atomic radii (crystal, Å)	Corresponding cations	Ionic radii (Å)
Li	1.52	Li <sup>+</sup>	0.59
Na	1.86	Na <sup>+</sup>	0.99
K	2.31	K <sup>+</sup>	1.33
Mg	1.60	Mg <sup>2+</sup> Ba <sup>2+</sup>	0.65
Ва	2.22		1.35
Al	1.43	Al <sup>3+</sup>	0.50
Pb	1.75	Pb <sup>2+</sup>	1.32

#### **Comparative Sizes of Atoms and their Anions**

Atom	Atomic radii (covalent, Å)	Corresponding anions	Ionic radii (Å)
F	0.72	F	1.36
Cl	0.99	Cl <sup></sup>	. 1.81
Br	1.14	Br <sup></sup>	1.96
О	0.73	$O^{2-}$	1.40
S	1.04	S <sup>2-</sup>	1.84
N	0.75	N <sup>3</sup>	1.71
P	1.10	P <sup>3-</sup>	2.12

In any particular group, the ions (cations or anions) increase in size on moving from top to bottom. This is due to an increase in the number of shells. For example,

The size of the cations of the same element decreases with the increase of positive charge. For example,  $Pb^{4+}$  is smaller in size than  $Pb^{2+}$ ;  $Sn^{4+}$  is smaller in size than  $Sn^{2+}$ ;  $Fe^{3+}$  is smaller in size than  $Fe^{2+}$ .

$$Fe^{3+}$$
 0.67 Å  $Cu^{2+}$  0.72  $Co^{3+}$  0.64  $Fe^{2+}$  0.82 Å  $Cu^{+}$  0.96  $Co^{2+}$  0.82

This can be explained on the basis of Z/e ratio  $\left(\frac{\text{Nuclear charge}}{\text{No. of electrons}}\right)$ . Whenever Z/e ratio increases, the size decreases and when Z/e ratio decreases, the size increases.

Na Na\* Cl Cl Fe<sup>2+</sup> Fe<sup>3+</sup> 
$$Z/e$$
  $\frac{11}{11} = 1.0$ ;  $\frac{11}{10} = 1.1$ ;  $\frac{17}{17} = 1.0$ ;  $\frac{17}{18} = 0.95$ ;  $\frac{26}{24} = 1.08$ ;  $\frac{26}{23} = 1.13$  So Na\* < Na Cl > Cl Fe<sup>3+</sup> < Fe<sup>2+</sup>

Isoelectronic species (ions or atoms) are those which have same number of electrons. For such species the size decreases with an increase of atomic number. This is illustrated in the following table:

Atom or Ion	Atomic number Z	No. of electrons <i>e</i>	Z/e ratio	Size in Å
C <sup>4-</sup> N <sup>3-</sup>	6	10	0.6	2.60
$N^{3-}$	7	10	0.7	1.71
O <sup>2-</sup>	8	10	0.8	1.40
F-	9	10	0.9	1.36
Ne	10	10	1.0	1.12
Na <sup>+</sup>	11	10	1.1	0.99
Mg <sup>2+</sup> Al <sup>3+</sup>	12	10	1.2	0.65
Al <sup>3+</sup>	13	10	1.3	0.50

H<sup>+</sup> and Cs<sup>+</sup> are the smallest and largest cations respectively.

H and I are the smallest and largest anions respectively.

#### **Conclusions**

- (i) The radius of cation (positive ion) is always smaller than that of the parent atom.
- (ii) The radius of anion (negative ion) is always larger than that of the parent atom.
- (iii) The ionic radii in a particular group increase in moving from top to bottom.
- (iv) In a set of species having the same number of electrons (isoelectronic), the size decreases as the charge on the nucleus increases.
- (v) The size of the cations of the same element decreases with the increase of positive charge.

# 1.14 IONISATION ENTHALPY OR IONISATION POTENTIAL

The electrons in an atom are attracted by the positive charge present on the nucleus. To remove an electron from an atom, energy has to be supplied to overcome the force of attraction towards nucleus. A quantitative measure of the tendency of an atom of an element to lose electron is given by its ionisation enthalpy. It is defined as the minimum amount of energy required to remove most loosely bound electron from an isolated atom in the gaseous state of an element so as to convert it into gaseous monovalent positive ion. It is also known as first ionisation enthalpy or energy. The process can be represented as:

$$M(g) \xrightarrow{\text{+energy}} M^+(g) + e$$

or 
$$M(g) + IE_1 \text{ or } *\Delta_i H_1 \longrightarrow M^+(g) + e$$

Ionisation enthalpy is also called as ionisation potential as it is the minimum potential difference in a discharge tube required to remove the most loosely bound electron from an isolated gaseous atom to form gaseous cation.

Ionisation enthalpy (or potential) is expressed either in terms of electron volts per atom (eV/atom) or kilocalories per mole (kcal mol<sup>-1</sup>) or kilojoules per mole (kJ mol<sup>-1</sup>).

1 electron volt (eV) per atom

$$= 3.83 \times 10^{-20}$$
 cal per atom  $= 1.602 \times 10^{-19}$  J per atom

$$= 3.83 \times 10^{-20} \times 6.023 \times 10^{23} \text{ cal mol}^{-1}$$

 $= 23.06 \text{ kcal mol}^{-1}$ 

= 
$$1.602 \times 10^{-19} \times 6.023 \times 10^{23} \text{ J mol}^{-1}$$

 $= 96.49 \text{ kJ mol}^{-1}$ 

 $\therefore$  1 eV per atom = 23.06 kcal mol<sup>-1</sup> = 96.49 kJ mol<sup>-1</sup>

Like the removal of first electron from isolated gaseous atom, it is possible to remove second, third and successive electrons from positive ions one after the other. The amounts of energies required are termed second, third, fourth ...... ionisation enthalpies respectively. These processes can be shown as:

$$M^{+}(g) + \Delta_{i}H_{2} \text{ or } IE_{2} = M^{2+}(g) + e$$
  
 $M^{2+}(g) + \Delta_{i}H_{3} \text{ or } IE_{3} = M^{3+}(g) + e$   
 $M^{3+}(g) + \Delta_{i}H_{4} \text{ or } IE_{4} = M^{4+}(g) + e$ 

It is observed that  $\Delta_i H_2(IE_2)$  has higher value than  $\Delta_i H_1(IE_1)$ .  $\Delta_i H_3$  is higher than  $\Delta_i H_2$  and so on, *i.e.*,

$$\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3 < \Delta_i H_4$$

The successive ionisation enthalpies of first ten elements are given in the following table:

### Successive Ionisation Energies of the First Ten Elements (kJ/mol)\*\*

Element	Electronic configuration	First	Second	Third	Fourth	Fifth	Sixth	Seventh
Н	$1s^1$	1312	,					
He	$1s^2$	2372	5250					
Li	$1s^2$ , $2s^1$	520	7298	11,815		•		
Be	$1s^2$ , $2s^2$	899	1757	14,848	21,006		*	
В	$1s^2$ , $2s^22p^1$	801	2427	3660	25,025	32,826		
C	$1s^2$ , $2s^22p^2$	1086	2353	4620	6222	37,829	47,276	
N	$1s^2$ , $2s^22p^3$	1402	2857	4578	7475	9445	53,265	64,358
O	$1s^2$ , $2s^22p^4$	1314	3388	5300	7469	10,989	13,326	15,160
F	$1s^2$ , $2s^22p^5$	1681	3374	6020	8407	11,022	15,164	17,867
Ne	$1s^2$ , $2s^22p^6$	2081	3952	6122	9370	12,177	15,238	19,998

<sup>\*\*</sup>Ionisation energies to the right of a vertical line correspond to removal of electrons from the core of the atom.

The increase in the values of successive ionisation enthalpies can be explained on the basis that effective nuclear charge increases from M(g) to  $M^{n+}(g)$ , *i.e.*, electrostatic attraction between the nucleus and the remaining electrons in the cation (especially the outermost electron in the cation)

increases. This requires higher energy to remove the electron from the cation in comparison to neutral atom. The energy increases as the charge on the cation increases gradually. Thus, successive ionisation enthalpies have higher values.

<sup>\*</sup>H represents enthalpy and ΔH, change in enthalpy. It is given positive sign if energy is required and negative sign if it is released.

an **endoergic** process and will be given a positive sign. Similarly, higher electron gain enthalpies are positive. For example, when an electron is added to an oxygen atom to form O<sup>-</sup> ion, energy is released. However, when second electron is added to O<sup>-</sup> ion to form O<sup>2-</sup> ion, energy is absorbed.

$$O(g) + e \longrightarrow O^{-}(g)$$
; 1st  $\Delta H_{eg} = -141 \text{ kJ mol}^{-1}$  (Energy released)  
 $O^{-}(g) + e \longrightarrow O^{2-}(g)$ ; 2nd  $\Delta H_{eg} = +780 \text{ kJ mol}^{-1}$  (Energy absorbed)

Similarly for sulphur atom, the second electron gain enthalpy is positive.

$$S(g) + e \longrightarrow S^{-}(g)$$
; 1st  $\Delta H_{eg} = -200 \text{ kJ mol}^{-1}$   
 $S^{-}(g) + e \longrightarrow S^{2-}(g)$ ; 2nd  $\Delta H_{eg} = +590 \text{ kJ mol}^{-1}$ 

The magnitude of electron affinity depends on a number of factors such as:

- **(i) Size of the atom :** Smaller the size of the atom, stronger is the attraction for the added electron towards nucleus. Thus, smaller the size of atom, greater is the electron affinity.
- **(ii) Nuclear charge:** Greater the nuclear charge, stronger is the attraction for the added electron towards nucleus. Thus, electron affinity increases as nuclear charge increases.
- (iii) Electronic configuration: The elements having stable configuration (half filled or fully filled valence subshells) have very little or no tendency to accept additional electron; hence, electron affinities are low or zero in these cases.

### Variation of Electron Gain Enthalpies in Periodic Table

In general, the electron gain enthalpy becomes less negative in going from top to bottom in a group and more negative in going from left to right in a period. However, electron gain enthalpy does not show a regular trend along a period or a group. The electron gain enthalpies of normal elements are given in the following table in kJ mol<sup>-1</sup>:

$\begin{array}{c} \text{Period} \ \downarrow \\ \text{Group} \rightarrow \end{array}$	1	2	13	14	15	16	17	18
1	H -73				,			He +48
2	Li	Be	B	C	N	O	F	Ne
	-60	+66	-83	-122	+31	-141	-328	+116
3	Na	Mg	Al	Si	P	S	Cl	Ar
	-53	+67	-50	-119	-74	-200	-349	+96
4	K	Ca	Ga	Ge	<b>A</b> s	Se	Br	<b>Kr</b>
	-48	-	-36	-116	-77	-195	-325	+96
5	Rb	Sr	In	Sn	Sb	Te	I	Xe
	-47	-	29	-120	-101	-1 <b>9</b> 0	-295	+77
6	Cs	Ва	T1	Pb	Bi	Po	At	Rn
	-46		-30	-101	-1 <b>1</b> 0	-174	-270	+68

From the table, the following trends are observed:

(i) The electron gain enthalpies, in general, become less negative in going down from top to bottom in a group. This is due to increase in size on moving down a group. This factor is predominant in comparison to other factor, *i.e.*, increase in nuclear charge.

(ii) The electron gain enthalpies of oxygen and fluorine, the members of the second period, have less negative values than the elements sulphur and chlorine of the third period.

This is due to small size of the atoms of oxygen and fluorine. As a result, there is a strong inter-electronic repulsion when extra electron is added to these atoms, *i.e.*, electron density is high and the addition of electron is not easy. Thus, the electron gain enthalpies of third period elements, sulphur and chlorine, have more negative values than corresponding elements oxygen and fluorine.

O 
$$-141 \text{ kJ mol}^{-1}$$
 F  $-328 \text{ kJ mol}^{-1}$   
S  $-200 \text{ kJ mol}^{-1}$  Cl  $-349 \text{ kJ mol}^{-1}$ 

Similar trend is observed in nitrogen and phosphorus.

- (iii) In general, electron gain enthalpy becomes more and more negative from left to right in a period. This is due to decrease in size and increase in nuclear charge as the atomic number increases in a period. Both these factors favour the addition of an extra electron due to higher force of attraction by the nucleus for the incoming electron.
- (iv) Electron gain enthalpies of some of the members of alkaline earth metals, noble gases and nitrogen are positive.

This is because they have stable configurations. Alkaline earth metals have stable configurations due to completely filled ns orbital while nitrogen has extra stability due to half filled p-orbitals  $(1s^2, 2s^2 2p_x^1 2p_y^1 2p_z^1)$ , i.e., symmetrical configuration. These atoms resist the addition of extra electron as they do not want to disturb their stability.

Noble gases have  $ns^2np^6$  configuration, *i.e.*, no place for incoming electron. In case the extra electron is to be accommodated, it will occupy its position on a new principal shell, *i.e.*, it will be weakly attracted towards nucleus. Such anion will be extremely unstable. Helium has also a stable  $1s^2$  configuration and cannot accommodate the incoming electron.

- (v) Halogens have highest negative electron gain enthalpies. Following two factors are responsible for this:
- (a) Small atomic size and high nuclear charge of halogens in a period.

(b) Halogens have the general electronic configuration of  $ns^2np^5$ , i.e., one electron less than stable noble gas  $(ns^2np^6)$  configuration.

Thus, halogens have a very strong tendency to accept an additional electron and their electron gain enthalpies are, therefore, high.

### Importance of Electron Gain Enthalpy

Certain properties of the elements can be predicted on the basis of values of electron gain enthalpies.

- (i) The elements having high negative values of electron gain enthalpy are capable of accepting electron easily. They form anions and thus form ionic (electrovalent) compounds. These elements are **electronegative** in nature.
- (ii) The elements having high negative electron gain enthalpies act as strong oxidising agents, for example, F, Cl, Br, O, S, etc.

On the basis of the general trend of ionisation enthalpy and electron gain enthalpy, the following properties can be predicted:

(i) Metallic nature decreases in a period while non-metallic nature increases. Metallic nature increases in a group while non-metallic nature decreases. The arrow  $(\downarrow)$  represents a group and  $(\rightarrow)$  represents a period.

$$\begin{array}{c|c} & Metallic & Non-metallic \\ Metallic & \longrightarrow Decreases \\ (Electro +ve) & Decreases \\ & Increases & Decreases \\ \end{array}$$

(ii) Stability of metal increases while activity of the metal decreases in a period and in a group stability decreases while activity increases.

This trend is observed especially in IA, IIA and IIIA elements.

(iii) The basic nature of the oxides decreases in a period while acidic nature increases. In a group, basic nature increases while acidic nature decreases.

### 1.16 ELECTRONEGATIVITY

This is the property of a bonded atom. The relative tendency of an atom to attract the shared electron pair towards itself is called electronegativity. Electron gain enthalpy and electronegativity both measure the power of attracting electrons but electron gain enthalpy is concerned with an isolated gaseous atom while electronegativity is concerned with the atom in combination. Electronegativity concept was introduced by Pauling in 1932. An arbitrary value of 4.0 has been assigned to fluorine (most electronegative element) and the electronegativities of other elements have been calculated against this standard by the application of following formula:

$$X_A - X_B = 0.208[E_{A - B} - \frac{1}{2}(E_{A - A} + E_{B - B})]^{\frac{1}{2}}$$

where  $X_A$  and  $X_B$  are the electronegativities of two atoms A and B and  $E_{A\_B}$ ,  $E_{A\_A}$  and  $E_{B\_B}$  are bond energies of molecules A-B,  $A_2$  and  $B_2$ , respectively in kcal mol<sup>-1</sup> or  $X_A-X_B=0.102$   $[E_{A\_B}-\frac{1}{2}(E_{A\_A}+E_{B\_B})]^{\frac{1}{2}}$ , if the bond energies are taken in kJ mol<sup>-1</sup>.

Mulliken regarded electronegativity as the average value of ionisation potential and electron gain enthalpy of an atom when both are taken in electron volts.

Electronegativity = 
$$\frac{IP + EA}{2}$$

[IP = Ionisation enthalpy; EA = Electron gain enthalpy]

However, it was found that Mulliken values were 2.8 times greater than Pauling values.

Thus, electronegativity in Pauling scale = 
$$\frac{IP + EA}{2 \times 2.8}$$
$$= \frac{IP + EA}{5.6}$$

Electronegativity of an atom on Pauling scale if the values are taken in kcals per mole =  $\frac{IP + EA}{2 \times 2.8 \times 23.06}$ 

Electronegativity of an atom on Mulliken scale if the values of IP and EA are taken in kJ mol<sup>-1</sup> =  $\frac{IP + EA}{2 \times 96.48}$ 

Thus, electronegativity of an atom on Pauling scale

$$=\frac{IP + EA}{2 \times 96.48 \times 2.8} = \frac{IP + EA}{540}$$

On Allred and Rochow scale, the electronegativity is calculated by applying the following formula,

$$X_A = 0.744 + \frac{0.359 Z_{\text{effective}}}{r^2}$$

where  $Z_{\text{effective}}$  = Effective nuclear charge at periphery of element A.

r = radius of the element A in Å.

In general, the electronegativity values are high for smallest elements and low for bigger atoms.

The electronegativity values of representative elements on the pauling scale are given in the following table:

Group →	1 IA	2 <b>IIA</b>	13 IIIA	14 IVA	15 VA	16 <b>VIA</b>	17 <b>VIIA</b>	
I period	Н							1
	2.1							-
II period	Li	Be	В	C	N	О	F	
	1.0	1.5	2.0	2.5	3.0	3.5	4.0	
III period	Na	Mg	Al	Si	P	, , <b>S</b>	Cl	
*	0.9	1.2	1.5	1.8	2.1	2.5	3.0	
IV period	K	Ca	Ga	Ge	As	Se	Br	
	0.8	1.0	1.6	1.8	2.0	2.4	2.8	
V period	Rb	Sr	In	Sn	Sb	Te	I	. 4
	0.8	1.0	1.7	1.8	1.9	2.01	2.5	ses
VI period	Cs	Ba	Tl	Pb	Bi	Po	Αt	rea
- •	0.7	0.9	1.8	1.9	1.9	1.76	2.2	Decreases
						$\longrightarrow$ Inc	reases	

In a period from left to right, the value of electronegativity increases while in a group from top to bottom, the value of electronegativity decreases.

The electronegativity of any given element is not constant but is dependent on the following factors:

(i) State of hybridization: For example, in the case of carbon, electronegativity decreases from sp state to  $sp^3$  state.

$$sp > sp^2 > sp^3$$
 electronegativity decreases

(ii) Oxidation state of the element: With increase of oxidation state, electronegativity increases. Fe<sup>3+</sup> (EN = 1.96) has higher electronegativity than Fe<sup>2+</sup> (EN = 1.83).

### Importance of Electronegativity

The following predictions can be made from values of electronegativity:

- (i) Nature of the bond between two atoms can be predicted by the electronegativity difference of the two atoms.
- (a) When difference  $X_A X_B = 0$ , i.e.,  $X_A = X_B$ , the bond is purely covalent. For example,  $H_2$ ,  $Cl_2$ ,  $O_2$  and  $N_2$  molecules are purely covalent and non-polar.
- (b) The difference  $X_A X_B$  is small, *i.e.*,  $X_A > X_B$ , the bond is polar covalent.
- (c) The difference  $X_A X_B$  is 1.9, the bond is 50% covalent and 50% ionic.
- (d) The difference  $X_A X_B$  is very high, the bond is more ionic and less covalent. The molecule will be represented in such case as  $BA(B^+A^-)$ .

Percentage ionic character may be calculated as:

Percentage of ionic character

$$=16(X_A - X_B) + 3.5(X_A - X_B)^2$$

where  $X_A$  and  $X_B$  represent electronegativity of bonded atoms A and B.

This relation was given by A.L. Allred (1961).

(ii) The elements having low values of electronegativity are metals while the elements having high values of

electronegativity are non-metals. Fluorine with highest electronegativity is the most non-metallic and caesium with lowest electronegativity is the most metallic element of the periodic table.

(iii)  $(X_O - X_A)$  difference predicts the nature of the oxides formed by the element A.  $X_O$  is electronegativity of oxygen.

 $X_O - X_A$  is large, the oxide shows basic nature (e.g., Na<sub>2</sub>O).  $X_O - X_A$  is small, the oxide shows acidic nature (e.g., SO<sub>2</sub>).

## Difference between Electron Gain Enthalpy and Electronegativity

Electron Gain Enthalpy	Electronegativity
1. It is the tendency of an isolated atom to attract electron.	It is the tendency of an atom in a combined state, i.e., in a molecule
	to attract the shared pair of electrons.
<ol><li>It can be measured experi- mentally.</li></ol>	It is a relative number and cannot be determined experimentally.
<ol><li>Its units are electron volts per atom or kilojoules per mole or kilocalories per mole.</li></ol>	It has no units but merely a number.
<ol> <li>It is a constant quantity for a particular element.</li> </ol>	Electronegativity of an element is not constant. It depends on a number of factors such as hybri- dised state, oxidation state, etc.
5. Its periodicity is not regular in a period or a group.	

# 1.17 SOME OTHER PROPERTIES IN WHICH PERIODICITY IS OBSERVED

(i) Atomic volume: Atomic volume increases in a group from top to bottom. The increase is due to the increase in the number of energy shells.

In a period from left to right, atomic volume varies cyclically, i.e., it decreases at first for some elements, becomes minimum in the middle and then increases. The following two factors explain this trend:

- (a) Atomic radii decrease due to increase of nuclear charge.
- (b) The number of valency electrons increases in a period. As to accommodate all the valency electrons, the volume increases. These two factors oppose each other. The effect of first factor is more on the left hand side and that of the second factor is more on the right hand side.

The maximum value of atomic volume (87) is observed in the case of francium (last member of alkali group).

(ii) Density: The density of the elements in solid state varies periodically with their atomic numbers. At first, the

density increases gradually in a period and becomes maximum somewhere for the central members and then starts decreasing afterwards gradually.

Li	Вe	В	С	N	0	F
0.5	1.8	2.3	2.2		-	
Na	Mg	Al	Si	P	S	Cl
1.0	1.7	2.7	2.3	1.8	2.1	-
K					Se	Br
0.9					4.8	3.1
Rb	*		•		Te	. I
1.5					6.2	4.9
Cs						
1.9						

In solids, osmium has the highest density (22.6) and in liquids, Hg has the highest density (13.6).

(iii) Melting and boiling points: The melting points of the elements exhibit some periodicity with rise of atomic number. It is observed that elements with low values of atomic volumes have high melting points while elements with high values of atomic volumes have low melting points. In general, melting points of elements in any period at first increase and become maximum somewhere in the centre and thereafter begins to decrease. The melting points of the elements of second and third periods are given in the table:

The boiling points of the elements also show similar trends, however, the regularities are not striking as noted in the melting points. The boiling points of the elements of third period are given below:

In moving down the group, the melting and boiling points do show regular gradation, however, the pattern of variation is different in different groups. For example, in alkali group, the melting and boiling points decrease in moving from top to bottom but among halogens, there is increase in moving from top to bottom.

Element	Li	Na	K	Rb	Cs
M.pt.(K)	454	370.8	335	312	302
B.pt.(K)	1609	1165	1063	973	943
Element	F	Cl	Br	I	
M.pt.(K)	53	172	266	386	
B.pt.(K)	85	238	332	456	

Tungsten has the maximum melting point (3683K) amongst metals and carbon has the highest melting point (4000K) amongst non-metals. Helium has the lowest melting point (3K). The metals Cs, Ga and Hg are known in liquid state at 303K.

### Periodicity in Chemical Properties

#### (I) VALENCY

The combining capacity of an element is termed the valency. The valency of an element is linked with the number of electrons present in the outermost energy shell of the atom. The electrons present in the outermost shell are, therefore, termed as Valence electrons.

In the case of representative elements, the valency is generally equal to either the number of valence electrons or equal to eight minus number of valence electrons. However, the transition elements show variable valency involving valence electrons and d electrons of the penultimate energy shell. The common valence of transition metals are either 2 or 3.

Variation in a period: In the case of representative elements, the number of valence electrons increases from 1 to 8 from left to right in a period.

Group	1	2	13	14	15	16	17	18
Number of valence electron	1 ns	2	3	4	5	6	7	. 8
Valence on hydrogen scale	1	2	3	4	3	2	1	0
Valence on oxygen scale	1	2	3	4	5	6	7	. 0

On hydrogen scale, the valency increases from 1 to 4 and then decreases from 4 to 0, while on oxygen scale, it increases from 1 to 7.

Variation in a group: In a group, all the elements have same number of valence electrons and hence, all the elements show same valency. For example, the elements of group 1 (alkali metals) show monovalency while the elements of group 2 (alkaline earth metals) show divalency.

### (II) NATURE OF OXIDES

In a period, the nature of the oxides varies from basic to acidic as stated earlier.

In a group, basic nature increases or acidic nature decreases. Oxides of the metals are generally basic and oxides

of the non-metals are acidic. The oxides of the metalloids are amphoteric. The oxides of Al, Zn, Sn, As and Sb are amphoteric. We can summarise that as the electronegativity of element increases, acidic character of oxides increases.

When an element forms a number of oxides, the acidic nature increases as the percentage of oxygen increases.

$N_2O$	Neutral	$P_2O_3$	يو ا		MnO	Basic
NO 🔍	Neutral	P <sub>2</sub> O <sub>4</sub>	attn ses	nature ases	$Mn_2O_3$	Basic
$N_2O_3$	S. Cure	$P_2O_5$	ic na reas	natu	$MnO_2$	Neutral
$ \begin{array}{c} N_2O_3\\NO_2 \end{array} $	nai	** .	ig i	di di	$MnO_3$	Acidic
$N_2O_5$	ומוכ מכת	,	[ ▼	Acidic	$Mn_2O_7$	Acidic
	Ac			1		

CO,  $N_2O$ , NO and  $H_2O$  are neutral oxides. The oxides  $CO_2$ ,  $N_2O_5$ ,  $P_2O_3$ ,  $P_2O_5$ ,  $SO_2$ ,  $SO_3$ ,  $Cl_2O_7$ , etc., are called acid anhydrides as these combine with water to form oxyacids.

$$CO_2 \longrightarrow H_2CO_3$$
  $P_2O_3 \longrightarrow H_3PO_3$   
 $SO_3 \longrightarrow H_2SO_4$   $N_2O_5 \longrightarrow HNO_3$   
 $P_2O_5 \longrightarrow H_3PO_4$   $Cl_2O_7 \longrightarrow HClO_4$   
 $N_2O_3 \longrightarrow HNO_2$   $SO_2 \longrightarrow H_2SO_3$ 

### (III) NATURE OF OXY-ACIDS

VII group HClO<sub>4</sub>

In a period, the strength of the oxy-acids formed by non-metals increases from left to right.

II period 
$$\xrightarrow{\text{H}_3\text{BO}_3}$$
  $\xrightarrow{\text{H}_2\text{CO}_3}$   $\xrightarrow{\text{HNO}_3}$  Strength increases

III period  $\xrightarrow{\text{H}_2\text{SiO}_3}$   $\xrightarrow{\text{H}_3\text{PO}_4}$   $\xrightarrow{\text{H}_2\text{SO}_4}$   $\xrightarrow{\text{HCIO}_4}$  Strength increases

In a group, the strength of the pxy-acids of non-metals decreases.

V group  $\xrightarrow{\text{HNO}_3}$   $\xrightarrow{\text{H}_3\text{PO}_4}$   $\xrightarrow{\text{H}_3\text{AsO}_4}$  Strength decreases

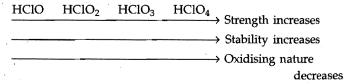
If a non-metal forms a number of oxy-acids, the strength increases with the increase of percentage of oxygen.

HBrO<sub>4</sub>

HIO<sub>4</sub>
Strength decreases

Sulphur forms two oxy-acids  $H_2SO_3$  and  $H_2SO_4$ . $H_2SO_4$  is stronger acid than  $H_2SO_3$ .

Chlorine forms a number of oxy-acids:



Greater is the oxidation state of central atom; more will be the acidic strength.

### (IV) NATURE OF HYDRIDES

The nature of the hydrides changes from basic to acidic in a period from left to right.

$NH_3$	$H_2O$	HF
Weak base	Neutral	Weak acid
$PH_3$	$H_2S$	HCl .
Very weak base	Weak acid	Strong acid

In a group, the acidic nature of the hydrides of non-metals increases. The reducing nature also increases but stability decreases from top to bottom.

HF HCl HBr HI	Strength of the acid increases
	Stability decreases
	Reducing nature increases

## (V) ANOMALOUS BEHAVIOUR OF THE ELEMENTS OF SECOND PERIOD

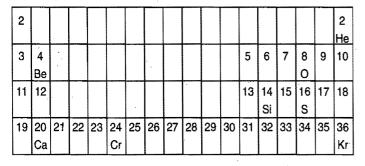
It has been observed that in the case of representative elements, the first element in each group, *i.e.*, lithium in the first group, beryllium in the second group and boron to fluorine in the groups 13 to 17, differ in many respects from the other members of their respective groups. The anomalous behaviour of the first member of each group is attributed to following reasons:

- (a) small atomic radius of the atom and ionic radius of its ion.
  - (b) high electronegativity.
  - (c) non-availability of *d*-orbitals in their valence shell.
- (d) tendency to form multiple bonds by carbon, nitrogen and oxygen.
  - (e) high charge/radius ratio.

The abnormal properties will be discussed in detail in respective groups.

## SOME SOLVED PROBLEMS

**Problem 1.** The diagram given below is a part of the periodic table. Study the table and answer the questions that follow:



- (i) Name two elements in the same group of the periodic table.
- (ii) Name a transition metal.
- (iii) Name an element whose oxide is basic.
- (iv) Name an element whose oxide has a very low melting point.
- (v) Name an element which reacts vigorously with water.
- (vi) Name an element which forms a colourless solid chloride  $XCl_2$ , where X = the element.
  - (vii) Name the element which is gaseous at room temperature.
  - (viii) Name a metallic element which has a high melting point.
- (ix) Name two elements which would react with each other to form a single compound.
- (x) Give the atomic number of an element which is an alkali metal.
- (xi) How many atoms of element-35 can combine with an atom of element-20?
  - (xii) Give the atomic number of an element which is inert.

### Solution:

- (i) The elements placed vertically one below another belong to the same subgroup. Thus, Be and Ca belong to the same subgroup.
- (ii) First transition series starts from element-21 and ends at element-30. Thus, chromium-24 is a transition metal.
- (iii) The oxides formed by the elements on left hand side of the periodic table are basic. Thus, calcium forms basic oxide.
- (iv) Sulphur forms a gaseous oxide whose melting point is low.
- (v) Alkali and alkaline earth metals react vigorously with water. Thus, calcium reacts vigorously with water.
- (vi) Calcium belongs to second group. It shows divalency and forms solid chloride of the type XCl<sub>2</sub>.
- (vii) Oxygen is known in gaseous state at room temperature.
- (viii) Transition metals have high melting points. Thus, chromium possesses high melting point.
  - (ix) Be and oxygen react together to form one oxide, BeO.

- (x) Alkali metals belong to first group. Thus, elements with atomic number 3, 11 and 19 are alkali metals.
- (xi) The element-35 is a halogen, its valency is one and the valency of element-20 (calcium) is two. Thus, one atom of element-20 combines with two atoms of element-35.
  - (xii) The atomic number of an inert gas is 36 (Kr).
- **Problem 2.** Among the elements with atomic numbers 9, 12 and 36, identify by atomic number of an element which is:
  - (a) highly electronegative
  - (b) an inert gas
  - (c) highly electropositive and give reasons for your choice.

### Solution:

The electronic configuration of the elements with atomic numbers 9, 12 and 36 are:

Atomic number 9; 2, 7

Atomic number 12; 2, 8, 2

Atomic number 36; 2, 8, 18, 8

The element with atomic number 9 can accept one more electron to have 8 electrons in the outermost orbit, thus it is an electronegative element.

The element with atomic number 12 loses two electrons to acquire inert gas configuration, thus it is electropositive in nature.

The element with atomic number 36 has 8 electrons in the outermost orbit, hence it has no tendency either to lose or accept electrons. Thus, it is an inert gas.

**Problem 3.** Two elements A and B have atomic number 16 and 19, respectively.

- (i) Write down the electronic configurations of A and B in terms of s, p, d and f.
  - (ii) Which element belongs to s-block of modern periodic table?
  - (iii) Which element belongs to p-block?
  - (iv) Which element is a powerful reducing agent?
- (v) Write down the formula of compound formed between A and B.

### Solution:

- (i)  $A = 1s^2, 2s^2 2p^6, 3s^2 3p^4$  (six electrons in valency shell).  $B = 1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$  (one electron in valency shell).
- (ii) B belongs to s-block as the last electron is accommodated on ns.
- (iii) A belongs to p-block as the last electron is accommodated on np.
- (iv) *B* has a tendency to lose valency electron easily, thus it acts as a powerful reducing agent.
- (v) The valency of B is 1 and that of A is 2. Thus, the formula of the compound formed is  $B_2A$ .

**Problem 4.** An element A has an atomic number 11.

- (i) Represent its electronic configuration.
- (ii) To which group of periodic table does it belong?

(iii) What is its valency?

(iv) Write the formula of its oxide.

#### Solution:

(i) Electronic configuration =  $1s^2$ ,  $2s^2 2p^6$ ,  $3s^1$ .

(ii) As one electron is present in the outermost energy shell, it belongs to first group of the periodic table.

(iii) Its valency is 1.

(iv) The formula of its oxide is  $A_2^{\circ}$ O.

Problem 5. Name the groups and periods of the elements having atomic number 18 and 26. What are the possible valencies of the above elements? [M.L.N.R. 1990]

#### Solution:

Electronic configurations of the elements are:

(A) At. no. 18

2, 8, 8

 $3s^{2} 3p$ 

(B) At. no. 26

2, 8, 8 + 6, 2

 $3d^6$ ,  $4s^2$ 

A belongs to third period and zero group.

B belongs to fourth period and eighth group.

*A* is an inert gas, its valency is zero while *B* is a transition metal. It can show variable valency. Its possible valencies are 2, 3 and 6.

**Problem 6.** The first ionisation energy of carbon atom is greater than that of boron atom, whereas reverse is true for the second ionisation energy. Explain.

#### Solution:

The electronic configurations of carbon and boron are as follows:

$$C: 1s^2, 2s^2 2p_x^1 2p_y^1 ; B: 1s^2, 2s^2 2p_x^1$$

Due to higher nuclear charge in carbon, the force of attraction towards valency electron is more in carbon atom and hence the first ionisation energy is greater than boron atom. After loss of one electron, the monovalent cations have the configurations as follows:

$$B^+: 1s^2, 2s^2 \; ; \; C^+: 1s^2, 2s^2 \; 2p_x^{\; 1}$$

The  $B^+$  configuration is a stable one and hence the removal of electron is difficult in comparison to  $C^+$ . Hence, second ionisation potential of boron is higher than carbon.

**Problem 7.** The formation of  $F^-(g)$  from F(g) is exothermic whereas that of  $O^{2-}(g)$  from O(g) is endothermic. Explain.

### Solution:

The addition of an electron to a neutral atom is an exoergic process.

$$F + e \longrightarrow F^- + \text{energy}$$
  
O +  $e \longrightarrow O^- + \text{energy}$  ...(i)

The addition of second electron to a monovalent anion  $O^-$ , as to make it  $O^{2-}$  is difficult because both have the same charge and experience a lot of repulsion. Thus, the addition of an electron to  $O^-$  requires energy to overcome the force of repulsion.

$$O^- + e + \text{energy} \longrightarrow O^{2-}$$
 ...(ii)

The energy absorbed in (ii) step is more than the energy released in the (i) step. Hence, the formation of  $O^{2-}$  from O is endothermic in nature.

**Problem 8.** (a) Why chlorine has higher negative electron gain enthalpy than F?

- (b) Why N has higher 1st ionisation enthalpy than O-atom?
- (c) Why Mg has higher 1st ionisation enthalpy than Al-atom?

#### Solution:

- (a) The size of fluorine atom is small and thus electron density is high. This resists the addition of electron, hence electron gain enthalpy of fluorine is less.
- (b) The electronic configurations of nitrogen and oxygen are as follows:

$$N: 1s^2, 2s^2 2p_x^1 2p_y^1 2p_z^1$$

O: 
$$1s^2$$
,  $2s^2 2p_x^2 2p_y^1 2p_z^1$ 

In N, *p*-orbitals are half filled and hence, its structure is stable. It requires more energy to remove an electron. Hence, the IE of nitrogen is higher than oxygen atom which has a less stable structure.

(c) The electronic configurations of Mg and Al are as follows:

$$Mg: 1s^2, 2s^2 2p^6, 3s^2$$

Al: 
$$1s^2$$
,  $2s^2$   $2p^6$ ,  $3s^2$   $3p^1$ 

It is difficult to remove an electron from 3s in comparison to 3p (3s paired and 3p singly occupied). Hence, IE of Mg is higher than Al.

**Problem 9.** The elements with atomic numbers 117 and 120 are yet to be discovered. In which family/group would you place these elements when discovered? Give their expected electronic configurations of the outermost shells and IUPAC names.

### Solution:

Atomic number	Name	Symbol	Electronic configuration	Group/family
117	Ununseptium	Uus	$7s^27p^5$	17/Halogen
120	Unbinilium	Ubn	8s <sup>2</sup>	2nd/Alkaline earth metals

**Problem 10.** Which of the following species will have the largest and smallest size?

$$Mg, Mg^{2+}, Al, Al^{3+}$$

Solution:

Mg and Al, both belong to same period.

Mg Al

Atomic number

Atomic size decreases from left to right across the period. Thus, Mg atom is larger in size than Al atom.

Cation is smaller than its neutral atom.  $Mg^{2+}$  ion is smaller than Mg atom and  $Al^{3+}$  ion is smaller than Al atom. Thus,

Al3+ ion is smallest and Mg atom is largest in size among the given species.

**Problem 11.** Arrange the following in order of increasing radii:

(i) 
$$I, I^+, I^-$$

(i) 
$$I, I^+, I^-$$
 (ii)  $C, N, Si, P$  (iii)  $O^{2-}, F^-, Ne, Mg^{2+}$  (iv)  $Fe, Fe^{2+}, Fe^{3+}$ 

### Solution:

(i)  $I^+ < I < I^-$ 

$$z/e$$
  $\frac{53}{52} \frac{53}{53} \frac{53}{54}$   $z/e$  decreases, hence size increases.

- (ii) N < C < P < Si
- (a) Effective nuclear charge in nitrogen is higher than in carbon, hence N < C.
- (b) Effective nuclear charge in phosphorus is higher than in silicon, hence P < Si.
- (c) C and Si both belong to same

C 
$$1s^2$$
,  $2s^22p^2$  (Two orbits)  
Si  $1s^2$ ,  $2s^22p^6$ ,  $3s^23p^2$  (Three orbits) C < Si

(iii) 
$$Mg^{2+} < Ne < F^- < O^{2-}$$

$$z/e \frac{12}{10} \frac{10}{10} \frac{9}{10} \frac{8}{10} z/e$$
 decreases, hence size increases.

(iv) 
$$Fe^{3+} < Fe^{2+} < Fe$$

$$z/e$$
  $\frac{26}{23}$   $\frac{26}{24}$   $\frac{26}{26}$   $z/e$  decreases, hence size increases.

Problem 12. Give the formula of a species that will be isoelectronic with the following atoms or ions:

(i) 
$$Ar$$
 (ii)  $F^-$  (iii)  $K^+$  (iv)  $Sr^{2+}$ 

### Solution:

Isoelectronic species are those which have same number of electrons.

- (i) Ar has 18 electrons. Therefore, the species P<sup>3-</sup>, S<sup>2-</sup>, Cl<sup>-</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, etc., are isoelectronic to Ar.
- (ii)  $F^-$  has 10 electrons. Therefore, the species  $N^{3-}$ , O<sup>2-</sup>, Ne, Na<sup>+</sup>, Mg<sup>2+</sup>, etc., are isoelectronic to F<sup>-</sup>.
- (iii) K<sup>+</sup> has 18 electrons. Therefore, the species P<sup>3-</sup>, S<sup>2-</sup>, Cl<sup>-</sup> , Ar,  $Ca^{2+}$ , etc., are isoelectronic to  $K^+$ . (iv)  $Sr^{2+}$  has 36 electrons. Therefore, the species  $Br^-$ , Kr,
- Rb<sup>+</sup>, etc., are isoelectronic to Sr<sup>2+</sup>.

### **Problem 13.** Answer the following:

- (i) How many elements can be accommodated in the present set up of the long form of periodic table?
  - (ii) What are superheavy elements?
- (iii) What would be IUPAC names and symbols with atomic numbers 126, 134 and 150?

### Solution:

(i) There are seven periods in the present long form of periodic table. In the last period 7s, 5f, 6d and 6p orbitals are to be filled, i.e., it can accommodate 32 electrons corresponding to 32 elements. Upto the end of sixth period 86 elements have been accommodated. Thus, the present long form of periodic table can accommodate 86 + 32 = 118elements.

- (ii) Elements with atomic number higher than 100 having high densities are called superheavy elements.
- (iii) The names and symbols of the elements with atomic numbers 126, 134 and 150 are:

Z	Name	Symbol
126	Unbihexium	Ubh
134	Untriquadium	Utq
150	Unpentnilium	Upn

**Problem 14.** Which of the elements Na, Mg, Si and P would have the greatest difference between the first and second ionisation enthalpies? Explain.

#### Solution:

Among these elements, sodium is an alkali metal and has the electronic configuration,  $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^1$ . Due to the presence of only one electron in the valence shell the first ionisation enthalpy is very low. After the removal of this electron, the Na<sup>+</sup> ion has inert gas configuration, i.e., 1s<sup>2</sup>, 2s<sup>2</sup>  $2p^6$ . To remove the electron from this configuration, very high energy is required. Therefore, the second ionisation enthalpy is expected to be very high. Consequently, the difference between first and second ionisation enthalpies would be greatest in sodium atom.

Problem 15. The ionisation enthalpy of lithium is 520 kJmol<sup>-1</sup>.Calculate the amount of energy required to convert 140 mg of lithium atoms in gaseous state into Li+ ion.

### Solution:

Mass of lithium = 140 mg  
= 
$$140 \times 10^{-3}$$
 g  
=  $14 \times 10^{-2}$  g

No. of moles of lithium = 
$$\frac{14 \times 10^{-2}}{7}$$
  
=  $2 \times 10^{-2}$  mole

Energy required to convert  $2 \times 10^{-2}$  mole atoms of lithium into Li<sup>+</sup> ions =  $520 \times 2 \times 10^{-2} = 10.4 \text{ kJ}$ 

**Problem 16.** The amount of energy when million atoms of iodine are completely converted into I ions in the vapour state according to the equation,

$$I_{(g)} + e \longrightarrow I_{(g)}^- \text{ is } 4.9 \times 10^{-13} \text{ J.}$$

Calculate the electron gain enthalpy of iodine in terms of  $kI \text{ mol}^{-1}$  and eV per atom.

### Solution:

The electron gain enthalpy of iodine is equal to the energy released when 1 mole of iodine atoms in vapour state are converted into I- ions

$$= \frac{4.9 \times 10^{-13} \times 6.023 \times 10^{23}}{10^6} = 29.5 \times 10^4 \text{ J} = 295 \text{ kJ}$$

Thus electron gain enthalpy of iodine =  $-295 \text{ kJ mol}^{-1}$ We know that 1 eV per atom =  $96.49 \text{ kJ mol}^{-1}$ 

:. Electron gain enthalpy of iodine in eV per atom

$$= -\frac{295}{96.49} = -3.06$$

**Problem 17.** Assign the position of the element having outer electronic configuration

(i)  $ns^2np^4$  for n=3

(ii)  $(n-1)d^2ns^2$  for n=4

(iii)  $(n-2)f^{7}(n-1)d^{1}ns^{2}$  for n=6

in the periodic table.

### Solution:

- (i) The element belongs to 3rd period (n = 3) and group 16 (10 + 2 + 4 = 16).
- (ii) The element belongs to 4th period and group 4(2 + 2 = 4).
- (iii) The element belongs to 6th period and group 3. It is a member of lanthanide series and placed with lanthanum.

**Problem 18.** The first and second ionisation enthalpies (kJ mol<sup>-1</sup>) of three elements I, II and III are given below:

	I	II	III
$\Delta_i H_1$	403	·5 <b>49</b>	1142
$\Delta_i H_2$	2640	1060	2080

Identify the element which is likely to be:

- (a) non-metal (b) an alkali metal
- (c) an alkaline earth metal.

#### Solution:

- (a) Element (III) is a non-metal because its  $\Delta_i H_1$  is highest among the three.
- (b) Element (I) is an alkali metal as its first ionisation enthalpy is lowest and second ionisation enthalpy is very high.
- (c) Element (II) is an alkaline earth metal because its first ionisation enthalpy is near to enthalpy of element (I) and second ionisation enthalpy is not very high.

**Problem 19.** How would you justify the presence of 18 elements in the 5th period of the periodic table?

### Solution:

Each period in the periodic table starts with the filling of a principal energy shell, *i.e.*, 5th period begins with the filling of 5s-orbital. Each period is completed by filling of *np*-orbitals, *i.e.*, 5th period is completed when 5p-orbitals attain 6 electrons. Between 5s and 5p-orbitals, 4d-orbitals are also filled as their energies are higher than 5s and lower than 5p-orbitals. Therefore, in fifth period the electrons can be filled only in 5s, 4d and 5p-orbitals, *i.e.*, 9 orbitals are filled accommodating 18 electrons. Hence, 5th period has 18 elements.

**Problem 20.** How would you react to the statement that electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds?

### Solution:

The statement that electronegativity of N on Pauling scale

is 3.0 in all nitrogen compounds is not correct as electronegativity of any atom is not a constant quantity. It varies with state of hybridization and the oxidation state of the element.

Problem 21. Answer the following:

- (a) Why do elements in a group show similar chemical properties?
- (b) Alkali metals have very high second ionisation enthalpy values. Why?

#### Solution:

- (a) In a group, all the elements have same number of electrons in the valence shell and the chemical properties mainly depend on the valence electrons. Therefore, the elements belonging to the same group show similar chemical properties.
- (b) The general electronic configuration of alkali metals is  $ns^1$ . By losing this electron, they acquire the configuration of the nearest noble gas element. It is a stable configuration and to remove the electron from this configuration is difficult, *i.e.*, requires a large amount of energy. Therefore, the second ionisation enthalpy values of alkali metals are high.

**Problem 22.** In terms of period and group, where would you locate the element with Z = 113? Give the IUPAC name and symbol of the element.

#### Solution:

The last member of 6th period is radon (Z = 86). In 7th period, 7s, 5f, 6d and 7p subshells are filled. The maximum capacity of these subshells is 2, 14, 10 and 6 respectively.

Atomic number difference with radon is = 113 - 86

Thus, the electronic configuration of the element, Z = 113, is

$$7s^2 5f^{14} 6d^{10} 7p^1$$

It, therefore, belongs to 7th period and group 13 of the periodic table. Its IUPAC name is Ununtrium and symbol is Uut.

Problem 23. What are the main factors due to which the ionisation enthalpy of the main group elements tend to decrease down the group?

#### Solution:

The ionisation enthalpy of the elements decreases down the group due to following two factors :

- (i) There is increase in the number of main energy shell in moving from element to element, *i.e.*, atomic size increases gradually at each succeeding element, thereby the force of attraction of the nucleus towards valence electrons decreases.
- (ii) There is increase in the magnitude of the screening effect on account of increase in the inner electrons from one member to another and thus, the force of attraction of the nucleus towards valence electrons decreases and hence, the ionisation enthalpy decreases.



## **SUMMARY AND IMPORTANT POINTS TO REMEMBER**



- Mendeleev's periodic table was based on atomic masses of the elements. When Mendeleev presented the periodic table, only 63 elements were known. He left 29 places in the table for unknown elements.
- 2. Modern Mendeleev periodic table is based on atomic numbers of the elements. The modern periodic law is:

"The physical and chemical properties of the elements are periodic function of their atomic numbers."

The horizontal row in the periodic table is called a **period** and vertical column is called a **group**. There are seven periods and nine groups in the modern Mendeleev periodic table.

3. The long or extended form of periodic table consists of seven periods and eighteen vertical columns (groups or families). The elements in a period have same number of energy shells, i.e., principal quantum number (n). These are numbered 1 to 7.

1st period	1 <i>s</i>	orbital filled	2 elements
2nd period	2s2p	orbitals filled	8 elements
3rd period	3s3p	orbitals filled	8 elements
4th period	4s3d4p	orbitals filled	18 elements
5th period	5s4d5p	orbitals filled	18 elements
6th period	6s4f5d6p	orbitals filled	32 elements
7th period	7s5f6d7p	orbitals filled	32 elements
	Total		*118 elements

At present 117 elements are known.

In a vertical column (group), the elements have similar valence shell electronic configuration and therefore exhibit similar chemical properties.

4. There are four blocks of elements: s-, p-, d- and f-blocks depending on the orbital which gets the last electron. The general electronic configuration of these blocks are:

s-block: [Noble gas] $ns^1$  or 2. However, hydrogen has  $1s^1$  configuration.

p-block : [Noble gas] $ns^2np^{1-6}$ 

d-block: [Noble gas]  $(n-1)d^{1-10}ns^1$  or 2

f-block: [Noble gas]  $(n-2)f^{1-14}(n-1)d^{0 \text{ or } 1}ns^2$ 

s-block elements occupy IA(1) and IIA(2) groups, i.e., extreme left portion of the periodic table.

*p*-block elements occupy IIIA(13), IVA(14), VA(15), VIA(16), VIIA(17) and VIIIA(18) groups, *i.e.*, right portion of the periodic table.

**d-block elements** occupy IIIB(3), IVB(4), VB(5), VIB(6), VIIB(7), VIIIB(8,9 and 10), IB(11) and IIB(12) groups, *i.e.*, central portion of the periodic table. There are four *d*-block series, *i.e.*, 3*d* series, 4*d* series, 5*d* series and 6*d* series, each consisting of ten elements, *i.e.*, in all, forty *d*-block elements are present in periodic table.

f-block elements are accommodated in two horizontal rows below the main periodic table, each row consists of 14

elements, i.e., 28 f-block elements are present in periodic table. The elements in first row are termed 4f-elements or rare earths or lanthanides while the elements of second row are termed 5f-elements or actinides.

- 5. The elements are broadly divided into three types:
  - (i) **Metals** comprise more than 78% of the known elements. s-block, d-block and f-block elements are metals. The higher members of p-block are also metals.
  - (ii) Non-metals are less than twenty. (C, N, P, O, S, Se, H, F, Cl, Br, I, He, Ne, Ar, Kr, Xe, Rn and Uuo are non-metals)
  - (iii) Elements which lie in the border line between metals and non-metals are called semimetals or metalloids. B, Si, Ge, As, Sb, Te, Po and At are regarded metalloids.
- 6. IUPAC has given a new scheme for assigning a temporary name to the newly discovered elements. The name is derived directly from the atomic number of the element. However, IUPAC has accepted the following names of the elements from atomic numbers 104 to 110.

Rutherfordium (Rf), Dubnium (Db), Seaborgium (Sg),
104 105 106

Bohrium (Bh), Hassium (Hs), Meitnerium (Mt),
107 108 109

Darmstadtium (Ds)

110

The temporary names of the elements discovered recently are:

Unununium (Uuu),

111

Ununtrium (Uut),

113

Ununquadium (Uuq),

114

Ununpentium (Uup),

115

Ununoctium (Uuo)

Ununhexium (Uuh),

116

Ununoctium (Uuo)

7. The recurrence of similar properties of the elements after certain definite intervals when the elements are arranged in the order of increasing atomic numbers in the periodic table is termed **periodicity**. The cause of periodicity is the repetition of similar electronic configuration of the atom in the valence shell after certain definite intervals. These definite intervals are 2, 8, 8, 18, 18 and 32.

Periodicity is observed in a number of properties which are directly or indirectly linked with electronic configuration.

- (i) Effective nuclear charge increases across each period.
- (ii) Atomic radii generally decrease across the periods.
- (iii) Atomic radii generally increase on moving from top to bottom in the groups.
- (iv) Atomic radius is of three types:

- (a) Covalent radius: It is half of the distance between the centres of the nuclei of two similar atoms joined by a single covalent bond. This is generally used for non-metals.
- (b) Crystal or metallic radius: It is half of the internuclear distance between two nearest atoms in the metallic lattice. It is generally used for metals.
- (c) van der Waals' radius: It is half of the internuclear distance between two nearest atoms belonging to two adjacent molecules in solid state.

van der Waals' radius > Metallic radius > Covalent radius

(for an atom)

- (v) Cations are generally smaller than anions.
- (vi) Cations are smaller and anions are larger than neutral atoms of the elements.

Cation < Neutral atom < Anion size size size

- (vii) Elements of 2nd and 3rd transition series belonging to same vertical columns are similar in size and properties due to lanthanide contraction.
- (viii) The first element is each group of the representative elements shows abnormal properties, i.e., differs from other elements of the group because of much smaller size of the atom.
  - (ix) The ions having same number of electrons but different nuclear charge are called isoelectronic ions.
     Examples,
    - (a)  $N^{3-}$ ,  $O^{2-}$ ,  $F^-$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Al^{3+}$
    - (b) P<sup>3-</sup>, S<sup>2-</sup>, Cl<sup>-</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Sc<sup>3+</sup>

In isoelectronic ions, the size decreases if z/e increases, *i.e.*, greater the nuclear charge, smaller is the size of the ion.

- (x) The energy required to remove the most loosely held electron from the gaseous isolated atom is termed ionisation enthalpy.
- (xi) Ionisation enthalpy values generally increase across the periods.
- (xii) Ionisation enthalpy values generally decrease down the group.
- (xiii) Removal of electron from filled and half filled shells requires higher energy. For example, the ionisation enthalpy of nitrogen is higher than oxygen. Be, Mg and noble gases have high values.

The following trend is observed in the first ionisation enthalpy of the elements of second and third periods. Second period Li < Be > B < C < N > O < F < Ne

or Li < B < Be < C < O < N < F < Ne

Third period Na < Mg > Al < Si < P > S < Cl < Ar or Na < Al < Mg < Si < S < P < Cl < Ar

- (xiv) Metals have low ionisation enthalpy values while nonmetals have high ionisation enthalpy values.
- (xv) Successive ionisation enthalpies of an atom have higher values.

 $IE_I < IE_{II} < IE_{III} \dots$ 

The largest jump in between first ionisation enthalpy and second ionisation enthalpy is in the case of alkali metals as  $ns^1$  configurations change into inert gas configurations.

The largest jump in between second ionisation enthalpy and third ionisation enthalpy is in the case of alkaline earth metals.

- (xvi) The enthalpy change taking place when an electron is added to an isolated gaseous atom of the element is called electron gain enthalpy. The first electron gain enthalpy of most of the elements is negative as energy is released in the process but the values are positive or near zero in case of the atoms having stable configuration such as Be, Mg, N, noble gases, etc.
- (xvii) Electron gain enthalpy becomes more negative from left to right in a period and less negative from top to bottom in a group.
- (xviii) Successive electron gain enthalpies are always positive.
- (xix) The elements with higher ionisation enthalpy have higher negative electron gain enthalpy.
- (xx) Electronegativity is the tendency of an atom to attract the shared pair of electrons towards itself in a bond.
- (xxi) Electronegativity increases across the periods and decreases down the groups.
- (xxii) Metals have low electronegativities and non-metals have high electronegativities.
- (xxiii) Metallic character decreases across the periods and increases down the group.
- (xxiv) Valency of an element belonging to s- and p-block (except noble gases) is either equal to the number of valence electrons or eight minus number of valence electrons.
- (xxv) The reducing nature of the elements decreases across the period while oxidising nature increases.
- (xxvi) The basic character of the oxides decreases while the acidic character increases in moving from left to right in a period.

### SOME IMPORTANT FACTS ABOUT ELEMENTS

- (i) Bromine is a non-metal which is liquid at room temperature.
- (ii) Mercury is the only metal that is liquid at room temperature.
- (iii) Gallium (m.pt. 29.8°C), caesium (m.pt. 28.5°C) and francium (m.pt. 27°C) are metals having low melting points.
- (iv) Tungsten (W) has the highest melting point (3380°C) among metals.
- (v) Carbon has the highest melting point (4100°C) among non-metals.
- (vi) Oxygen is the most abundant element on the earth.
- (vii) Aluminium is the most abundant metal.
- (viii) Iron is the most abundant transition metal.

- (ix) Highest density is shown by osmium (22.59 g cm<sup>-3</sup>) or iridium (22.61 g cm<sup>-3</sup>).
- (x) Lithium is the lightest metal. Its density is  $0.54 \text{ g cm}^{-3}$ .
- (xi) Silver is the best conductor of electricity.
- (xii) Diamond (carbon) is the hardest natural substance.
- (xiii) Francium has the highest atomic volume.
- (xiv) Boron has the lowest atomic volume.
- (xv) The most abundant gas in atmosphere is nitrogen.
- (xvi) Fluorine is the most electronegative element.
- (xvii) Chlorine has the maximum negative electron gain enthalpy.
- (xviii) Helium has the maximum ionisation enthalpy.
- (xix) Caesium or francium has the lowest ionisation enthalpy.
- (xx) Helium and francium are smallest and largest atoms respectively.
- (xxi) H and I ions are the smallest and largest anions respectively.
- (xxii) H<sup>+</sup> and Cs<sup>+</sup> ions are the smallest and largest cations respectively.
- (xxiii) Caesium is the most electropositive element.
- (xxiv) Element kept in water is phosphorus, P<sub>4</sub> (white or yellow).
- (xxv) Elements kept in kerosene oil are Na, K, Rb, Cs, etc.
- (xxvi) Iodine is the element which sublimes.
- (xxvii) Hydrogen is the most abundant element in the universe.
- (xxviii) Only ozone is the coloured gas with garlic smell.
- (xxix) Metalloids have electronegativity values closer to 2.0.
- (xxx) First synthetic (i.e., man-made) element is technetium (At. no. 43).
- (xxxi) Most poisonous metal-Plutonium.
- (xxxii) Rarest element in earth's crust-Astatine.
- (xxxiii) The elements coming after uranium are called transuranic elements. The elements with Z=104-116, and 118 are called transactinides or superheavy elements. All these elements are synthetic, *i.e.*, manmade elements. These are radioactive elements and not found in nature.
- (xxxiv) The elements ruthenium (Ru), germanium (Ge), polonium (Po), francium (Fr) and americium (Am) were named in honour of the countries named Ruthenia (Russia), Germany, Poland, France and America, respectively.

The Swedish town of Ytterby has the distinction of having four elements named after it. These elements are : erbium (Er), ytterbium (Yb), yttrium (Y) and terbium (Tb). An element has been named californium (Cf) after an American state california. Few elements have been named after some famous scientists/people but none of scientist/people discovered the element named after them. These elements are :

- 1. Samarium (Sm)
  2. Gadolinium (Gd)
  3. Curium (Cm)
  4. Einsteinium (Es)
  5. Fermium (Fm)
  6. Mendelevium (Md)
  7. Nobelium (No)
  8. Lawrencium (Lr)
  9. Rutherfordium (Rf)
  10. Seaborgium (Sg)
  11. Bohrium (Bh)
  12. Meitnerium (Mt)
- 13. Röntgenium (Rg)

The following elements have been named after planets and stars.

- 1. Mercury (Hg) 2. Uranium (U)
  3. Neptunium (Np) 4. Plutonium (Pu)
  5. Titanium (Ti) 6. Zirconium (Zr)
- 7. Cerium (Ce)
- (xxxv) The members of the actinide series are radioactive and majority of them are not found in nature.
- (xxxvi) The element rutherfordium (Rf, 104) is also called Kurchatovium (Ku) and element dubnium (Db, 105) is also called hahnium.
- (xxxvii) Promethium (Pm, 61) a member of lanthanide series is not found in nature. It is a synthetic element.
- (xxxviii) Special names are given to the members of these groups in periodic table.

Group 1	or	ΙA	Alkali metals
Group 2	or	IIA	Alkaline earth metals
Group 15	or	VA	Pnictogens
Group 16	or	VIA	Chalcogens
Group 17	or	VIIA	Halogens
Group 18	or	VIIIA	Inert or noble gases
· · ·		(zero)	
Group 11	or	IB	Coinage metals

- (xxxix) Element having maximum number of isotopes—Sn (10 isotopes)
  - (xL) Least conductor among metals Pb (Lead)
  - (xLi) Heaviest naturally occurring element <sup>238</sup><sub>92</sub>U
  - (xLii) Liquid radioactive element -- Fr
- (xLiii) Element with highest tensile stress B
- (xLiv) Number of gaseous elements in the periodic table = 12  $(H_2, He, N_2, O_2, F_2, Cl_2, Ne, Ar, Xe, Kr, Rn and Uno)$
- (xLv) Most malleable metal Au
- (xLvi) Carbon has the maximum tendency for catenation.
- (xLvii) Out of 117 known elements, 90 are found in nature. These are from atomic numbers 1 to 92 with the exception of technetium (<sub>43</sub>Tc-a transition element) and promethium (<sub>61</sub>Pm-a member of lanthanide series). Traces of two posturanic elements neptunium (At. No. 93) and plutonium (At. No. 94) are found in nature in pitchblende ore.

# -•••- PRACTICE PROBLEMS -•••-

### Subjective Type Questions

- 1. Answer the following:
  - (a) Name the scientist who presented 'Law of octave'.
  - (b) Name the scientist who presented modified periodic law
  - (c) What is the basis for modern Mendeleev's periodic table and long form of periodic table?
  - (d) Name the anomalous pairs.
  - (e) Name the pairs showing a diagonal relationship.
  - (f) What are inner-transition elements?
  - (g) How many elements are present in each of the 3d, 4d and 5d-series?
  - (h) Which is the longest period in the long form of periodic table?
  - (i) Which is the shortest period in the long form of periodic table?
  - (j) How many incomplete periods are there in the long form of periodic table?
  - (k) Write the general electronic configuration of *d*-block elements.
  - (l) Write the general electronic configuration of *f*-block elements.
  - (m) Which element has the highest ionisation enthalpy value?
  - (n) Which element has the highest negative electron gain enthalpy value?
  - (o) Which element has the highest electronegativity?
  - (p) For what type of ions the ionic radius is less than the atomic radius?
  - (q) What are the units of ionisation enthalpy or electron gain enthalpy?
  - (r) Name the species (atoms or ions) having same number of electrons.
  - (s) Name three elements that exist in liquid state.
  - (t) How many more elements are to be discovered to complete the last period of the periodic table?
  - (u) How many metals and non-metals are known?
  - (v) Name the extreme left and extreme right groups of the extended form of the periodic table.
  - (w) What name is given to the elements belonging to third period of Mendeleev's periodic table?
  - (x) How many inner-transition elements are known?
- 2. Arrange the following in increasing order of the property indicated:
  - (i) F, Cl, Br and I (electron gain enthalpy) [I.I.T. 1993]
  - (ii)  $Mg^{2+}$ ,  $O^{2-}$ ,  $Na^{+}$ ,  $F^{-}$  and  $N^{3-}$  (ionic size) [I.I.T. 1991]
  - (iii) Cl, S<sup>2-</sup>, Ca<sup>2+</sup> and Ar (size)
  - (iv) Mg, Al, Si and Na (ionisation enthalpy)
  - (v) Br+, Br and Br- (size)
  - (vi) Pb, Pb<sup>2+</sup> and Pb<sup>4+</sup> (size)
  - (vii) HCl, HF, HI and HBr (acid strength)

- (viii) I<sub>2</sub>, F<sub>2</sub>, Br<sub>2</sub> and Cl<sub>2</sub> (reactivity)
  - (ix) Li, Be and B (ionisation enthalpy)
  - (x) Li, Na, K, Rb and Cs (hydrated radii)
  - (xi) SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub> and Cl<sub>2</sub>O<sub>7</sub> (acidic nature)
- (xii) F, Cl, Br and I (electronegativity)
- (xiii) Na, Cu and Zn (electropositive character)
- (xiv) Na, Al, Fe and Pb (density)
- (xv) C, N, O and F (2nd ionisation enthalpy)
- 3. With reference to periodic table, indicate:
  - (a) an element that is in group IIIA and third period.
  - (b) an element with an atomic number greater than 16 and chemically similar to the element with atomic number 10.
  - (c) first transition element of fourth period.
  - (d) the inert gases placed in the 2nd and 5th period.
  - (e) the group which accommodates lanthanides and actinides.
  - (f) the group all members of which are metals.
  - (g) position of most electropositive element.
  - (h) position of most electronegative element.
  - (i) the group to which most abundant element belongs.
  - (j) the groups of s-block elements.
- 4. (a) Group the following elements (atomic numbers given) into various blocks noted below:
  - 12, 19, 17, 25, 31, 42, 54, 23, 38
  - (i) s-block (ii) p-block (iii) d-block
  - (b) Which of the following are transition elements? K, Mn, Ca, Cs, Fe, Cu, Pb
  - (c) In how many blocks have the elements of long form of periodic table been divided? Name them.
  - (d) The electronic configurations of some of the elements are given below:
    - $(A) \ 1s^2, \ 2s^2 \ 2p^6, \ 3s^2 \qquad (B) \ 1s^2, \ 2s^2 \ 2p^6 \qquad (C) \ 1s^2, \ 2s^2 \ 2p^3$
    - (D)  $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^1$  (E)  $1s^2$ ,  $2s^2$   $2p^5$
    - (i) Name the elements.
    - (ii) Which of these has low ionisation enthalpy?
    - (iii) Which is a halogen?
    - (iv) Which is an alkali metal?
    - (v) Which is an inert gas?
- (a) From among the elements, choose the following:
   Cl, Br, F, O, Al, C, Li, Cs and Xe
  - (i) the element with highest electron gain enthalpy.
  - (ii) the element with lowest ionisation enthalpy.
  - (iii) the element whose oxide is amphoteric.
  - (iv) the element which has smallest radius.
  - (v) the element whose atom has 6 electrons in the outermost shell.
  - (vi) the element which belongs to zero group.
  - (vii) the element which forms largest number of compounds.
  - (viii) the element which shows diagonal relationship with Mg.

- (ix) the element which is in liquid state under ordinary atmospheric conditions.
- (b) The elements Na, Mg, Al, Si, P, S, Cl and Ar are arranged in the periodic table in the increasing order of their atomic numbers.
  - (i) Which element is the most electronegative?
  - (ii) Which element is the most electropositive?
  - (iii) Which element is the least reactive?
  - (iv) Which elements are gases at room temperature?
  - (v) Which element is the most abundant metal?
  - (vi) Which element is the strongest oxidising agent?
  - (vii) Which element has the electronic configuration?  $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^2$   $3p_x^1$   $3p_y^1$   $3p_z^1$
  - (viii) Which element shows +6 oxidation state?
- (c) Pick up from the elements Na, Cl, Si and Ar.
  - (i) the element with highest ionisation enthalpy.
  - (ii) the element with highest electron gain enthalpy.
  - (iii) the element with smallest size.
  - (iv) the element with largest radius.
  - (v) the element with lowest ionisation enthalpy.
- (d) A, B and C are the elements of a short period of a periodic table containing one, two and three electrons in their outermost shell, respectively.

Arrange A, B and C in the increasing order of:

- (i) their ionisation enthalpy
- (ii) basic character of their oxides
- (iii) covalent character in their chlorides and
- (iv) melting points of their chlorides.
- 6. (a) Give the electronic configuration of third alkali metal.
  - (b) Give the electronic configuration of fifth element of first transition series.
  - (c) Give the electronic configuration of ninth element of first transition series.
  - (d) Give the names and atomic numbers of the first and last members of the lanthanide series.
  - (e) Give the names and atomic numbers of the first and last members of the actinide series.

#### 7. Answer the following:

- (a) Name of the groups of elements classified as *s-*, *p-* and *d-*blocks.
- (b) In terms of electronic configuration, what the elements of a given period and a group have in common?
- (c) Name the groups whose elements are called representative elements.
- (d) Write the general electronic configuration of s-, p-, d- and f-block elements.

#### 8. Explain:

- (a) Mg<sup>2+</sup> ion is smaller than O<sup>2-</sup> ion although both have same electronic configuration.
- (b) Why nitrogen has slightly positive electron gain enthalpy?
- (c) Sulphur has more negative electron gain enthalpy than oxygen.
- (d) In a period of normal elements, which element has lowest ionisation enthalpy and which element has highest enthalpy?

- 9. The element 119 has not been discovered. What would be IUPAC name and symbol for this element? On the basis of the periodic table, predict the electronic configuration of this element and also the formula of its most stable chloride and oxide.
- 10. Predict the formulae of stable binary compounds that would be formed by the following pairs of elements:
  - (a) element 114 and fluorine
  - (b) element 120 and oxygen.
- 11. Write short notes on:
  - (i) Döbereiner's triads
  - (ii) Law of octaves
  - (iii) Lother Meyer's curve
  - (iv) The periodic law
  - (v) Groups and periods in modern Mendeleev's periodic table
  - (vi) Groups and periods in extended form of periodic table
  - (vii) Representative elements
  - (viii) Transition elements
  - (ix) Lanthanides
  - (x) Actinides
  - (xi) Defects of Mendeleev's periodic table
  - (xii) Merits of extended form of periodic table
  - (xiii) Isoelectronic species
  - (xiv) Screening effect
  - (xv) Effective nuclear charge
  - (xvi) Ionisation enthalpy
  - (xvii) Electron gain enthalpy
  - (xviii) Electronegativity
  - (xix) Covalent radii
  - (xx) Ionic radii

### 12. Explain the following:

(i) There are only 14 lanthanides and only 14 actinides.[Hint: In lanthanides and actinides, the differentiating

int: In lanthanides and actinides, the differentiating electron enters to (n-2)f-subshell. The maximum capacity of f-subshell is of 14 electrons. Thus, there are only 14 lanthanides  $(4f^{1-14})$  and only 14 actinides  $(5f^{1-14})$ .]

(ii) Why argon (at. mass 39.94) has been placed before potassium (at. mass 39.10) in the periodic table?

[M.L.N.R. 1990]

- [Hint: In modern periodic table, elements have been placed in order of their increasing atomic numbers.

  The atomic number of argon is 18 and that of potassium is 19. Thus, argon has been placed before potassium.]
- (iii) 3d, 4d and 5d series consists of 10 elements each.
  - [Hint: In 3d, 4d and 5d series, the differentiating electron enters to (n-1)d-subshell. The maximum capacity of d-subshell is of 10 electrons. Thus, there are 10 elements each in 3d, 4d and 5d series  $[(n-1)d^{1-10}]$ .]
- (iv) There are 2, 8 and 8 elements in first, second and third periods of periodic table respectively.
  - [Hint: In first period 1s is completed. Its capacity is of two electrons. In second period 2s 2p and in third period 3s 3p are completed. The capacity of these shells is of 8 electrons each. Thus, 2, 8 and 8

elements are present in first, second and third periods respectively.]

(v) Why f-block elements are so called?

[Hint: The differentiating electron enters to (n-2)f-subshell.]

(vi) Why zero group elements are inert?

[Hint: Zero group elements are inert because they have completely filled outermost shells. Neither they have a tendency to lose or gain or share electron/ electrons with other elements.]

(vii) The radius of a cation is lesser than atom while that of an anion is greater than the atom.

[Hint: In a cation, the nuclear charge acts on lesser number of electrons and thus, the electron cloud contracts. Hence, the net result is decrease in size. In an anion, the nuclear charge acts on larger number of electrons and thus, the electron cloud expands. Hence, the net result is increase in size. This can also be explained on the basis of z/e ratio. In cation z/e ratio increases, hence size decreases while in an anion z/e ratio decreases and so the size increases.]

(viii) Why the second ionisation enthalpy of an element is higher than the first?

> [Hint: The electrostatic attraction increases in unipositive ion than in a neutral atom.]

(ix) First ionisation enthalpy of nitrogen is higher than the first ionisation enthalpy of oxygen.

[Hint: Nitrogen has stable configuration as p-orbitals are half filled.  $1s^2$ ,  $2s^2$   $2p^1_x$   $2p^1_y$   $2p^1_z$ . Hence, more energy is required to remove an electron.]

(x) Why are the electron gain enthalpies of halogens so

[Hint: The electron is easily accommodated as halogens acquire inert gas configuration after gaining the electron.]

(xi) Why noble gases have positive electron gain enthal-

[Hint: Noble gases have a stable electronic configuration. Hence, it is difficult to add the electron resulting in positive electron gain enthalpy.]

(xii) Why most of the compounds of the transition elements are coloured?

[Hint: The ions contain unpaired d-electrons.]

(xiii) Why the atomic radii of 5d transition elements is same as 4d transition elements?

> [Hint: The increase in size that arises due to period change is almost compensated by lanthanide contraction.]

(xiv) Chlorine can be converted into chloride ion easily as compared to fluoride ion from fluorine.

> [Hint: Chlorine has higher value of electron gain enthalpy as compared to fluorine.]

(xv) s-block elements are very active.

[Hint: s-block elements have low ionisation enthalpies and thus, easily form cations.]

(xvi) Why Be and Mg atoms do not impart colour in a

[Hint: Be and Mg atoms are comparatively smaller and their ionisation energies are very high. Hence, their electrons are not excited by the energy of the flame to higher energy state. Therefore, these elements do not give any colour in flame.]

(xvii) Why is potassium a strongly electropositive element? [Hint: The ionisation potential of potassium is low. Hence,

it can lose an electron easily. Therefore, it is strongly electropositive in nature.]

(xviii) Why alkali metals do not form dipositive ions?

[Hint: The alkali metals after loss of one electron achieve stable configuration of inert gases. The removal of second electron requires very high energy, hence, alkali metals do not form dipositive ions.]

13. How do the following properties vary in a period and in a group of periodic table?

(a) Covalent radii

(b) Ionic radii

(c) Ionisation enthalpy

(d) Electron gain enthalpy

(e) Electronegativity

(f) Metallic and non-metallic

14. Write down the main characteristics of:

(a) s-block elements

(b) p-block elements

(c) d-block elements

(d) f-block elements

15. Calculate the electronegativity of fluorine from the following data:

 $E_{H-H} = 104.2 \text{ kcal mol}^{-1}$ ,  $E_{H-F} = 134.6 \text{ kcal mol}^{-1}$ ,

 $E_{F-F} = 36.6 \text{ kcal mol}^{-1},$   $X_{H} = 2.1.$  [M.L.N.R. 1996]

Solution: Let the electronegativity of fluorine be X<sub>F</sub>. Applying Pauling equation,

$$X_{\rm F} - X_{\rm H} = 0.208 \left[ E_{\rm H - F} - \frac{1}{2} \left( E_{\rm F - F} + E_{\rm H - H} \right) \right]^{\frac{1}{2}}$$

In this equation, dissociation energies are taken in kcal mol<sup>-1</sup>.

$$X_{\rm F} - 2.1 = 0.208 \left[ 134.6 - \frac{1}{2} \left( 104.2 + 36.6 \right) \right]^{\frac{1}{2}} = 3.76$$

16. Calculate the electronegativity of carbon from the following

 $E_{H-H} = 104.2 \text{ kcal mol}^{-1}$ ,  $E_{C-C} = 83.1 \text{ kcal mol}^{-1}$ ,

 $E_{C-H} = 98.8 \text{ kcal mol}^{-1}, X_H = 2.1.$ 

Solution:

Let the electronegativity of carbon be XC. Applying Pauling equation,

$$X_{C} - X_{H} = 0.208 [E_{C-H} - \frac{1}{2} (E_{C-C} + E_{H-H})]^{\frac{1}{2}}$$

$$X_{C} - 2.1 = 0.208 [98.8 - \frac{1}{2} (83.1 + 104.2)]^{\frac{1}{2}}$$

$$X_{C} = 2.5$$

17. Ionisation enthalpy and electron gain enthalpy of fluorine are 17.42 and 3.45 eV respectively. Calculate the electronegativity of fluorine.

Solution:

According to Mulliken equation,

 $X = \frac{1E + Eg}{5.6}$  when both IE and Eg are taken in eV.

$$X_{\mathbf{F}} = \frac{17.42 + 3.45}{5.6} = 3.726$$

18. The electron gain enthalpy of chlorine is 3.7 eV. How much energy in kcal is released when 2g of chlorine is completely converted to Cl ion in a gaseous state?  $(1 \text{ eV} = 23.06 \text{ kcal mol}^{-1})$ 

Solution:

$$Cl + e \longrightarrow Cl^{-} + 3.7 \text{ eV}$$
  
35.5  $3.7 \times 23.06 \text{ kcal}$ 

:. Energy released for conversion of 2g gaseous chlorine into CI ions

$$= \frac{3.7 \times 23.06}{35.5} \times 2 = 4.8 \text{ kcal}$$

Calculate the electronegativity of silicon using Allred-Rochow method. Covalent radius of silicon is 1.175 Å. Solution:

Allred-Rochow equation is,

$$X = 0.359 \frac{Z_{eff}}{r^2} + 0.744$$

 $X = 0.359 \; \frac{Z_{\it eff}}{r^2} + 0.744$  ( $Z_{\it eff}$  is calculated on the basis of Slater's rules taking all the electrons.)

Electronic configuration of Si is  $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^2$   $3p^2$ .

$$Z_{eff} = 14 - (0.35 \times 4 + 0.85 \times 8 + 2 \times 1) = 3.80$$
  
 $X = 0.359 \frac{3.80}{(1.175)^2} + 0.744 = 1.73$ 

The first ionisation enthalpy of Li is 5.4 eV and the electron gain enthalpy of Cl is 3.6 eV. Calculate  $\Delta H$  in kcal mol<sup>-1</sup> for the reaction,

 $Li(g) + Cl(g) \longrightarrow Li^+ + Cl^-$ 

Carried out at such low pressure that resulting ions do not combine with each other.

#### Solution:

The overall reaction is written into two partial equations.

$$\text{Li}(g) \longrightarrow \text{Li}^+ + e$$
  $\Delta E_1 = 5.4 \text{ eV}$   
 $\text{Cl}(g) + e \longrightarrow \text{Cl}^ \Delta E_2 = -3.6 \text{ eV}$ 

$$\Delta H = \Delta E_1 - \Delta E_2 = 5.4 - 3.6 = 1.8 \text{ eV}$$

 $= 1.8 \times 23.06 \text{ kcal mol}^{-1} = 41.508 \text{ kcal mol}^{-1}$ 

- Calculate the electronegativity value of chlorine on Mulliken's scale, given that IP = 13.0 eV and EA = 4.0 eV.
- 22. Find the electronegativity of lead with the help of the given values. Screening constant ( $\sigma$ ) of Pb = 76.70, atomic number of lead = 82 and covalent radius of Pb = 5.3 Å.
- The ionisation enthalpies of atoms A and B are 400 and 300 kcal mol<sup>-1</sup> respectively. The electron gain enthalpies of these atoms are 80.0 and 85.0 kcal mol<sup>-1</sup> respectively. Prove that which of the atoms has higher electronegativity?

[Hint: 
$$X_A = \frac{400 + 80}{2 \times 62.5} = 3.84$$
;  $X_B = \frac{300 + 85}{2 \times 62.5} = 3.08$ ]

Ans. A

For the gaseous reaction,

 $\rightarrow$  K<sup>+</sup> + F<sup>-</sup>,  $\Delta H$  was calculated to be 19 kcal under conditions where the cations and anions were prevented by electrostatic separation from combining with each other. The ionisation enthalpy of K is 4.3 eV. What is the electron gain enthalpy of F?

[Hint: 
$$K \longrightarrow K^+ + e$$
  $\Delta E_1 = 4.3 \text{ eV}$   
 $F + e \longrightarrow F^ \Delta E_2 = - EeV$   
 $\frac{19.0}{23.06} = \Delta E_1 - \Delta E_2 = 4.3 - E$   
 $0.82 = 4.3 - E$   
 $E = 3.481$ 

25. How many Cl atoms can you ionise in the process  $Cl \longrightarrow Cl^+ + e$  by the energy liberated for the process  $Cl + e \longrightarrow Cl^{-}$  for one Avogadro number of atoms? Given IE = 13.0 eV and Eg = 3.60 eV.

[Hint: Let n atoms be ionised.

$$6.02 \times 10^{23} \times \text{Eg} = n \times \text{IE}$$

$$n = \frac{6.02 \times 10^{23} \times 3.60}{13} = 1.667 \times 10^{23}$$
]

26. Give the name and atomic number of the inert gas atom in which the total number of d-electrons is equal to the difference in numbers of total p and s-electrons.

[Hint: Inert gas atom is krypton. Its atomic number is 36. The electronic configuration of Kr-atom is:

$$1s^2$$
,  $2s^2$   $2p^6$ ,  $3s^2$   $3p^6$   $3d^{10}$ ,  $4s^2$   $4p^6$ 

Total s-electrons = 8

Total p-electrons = 18

Difference = 18 - 8 = 10

Total d-electrons = 10 ]

### Matching Type Questions

### Match the following:

- (A) (a) Normal element
- (i) Uranium
- (b) Noble gas
- (ii) Copper
- (c) Transition element (iii) Cerium (d) Lanthanide
  - (iv) Radon
- (e) Actinide
- (v) Potassium
- (B) (a) Fluorine
- (i) Highest negative electron gain enthalpy
- - (ii) Most electropositive element
- (b) Helium (c) Chlorine
- (iii) Most electronegative element
- (d) Caesium
- (iv) Strongest reducing agent in soln.
- (e) Lithium
- (v) Highest ionisation enthalpy
- (C) (a) s-block element
- (i) Sulphur
- (b) p-block element
- (ii) Argon
- (c) d-block element
- (iii) Neptunium
- (d) f-block element
- (iv) Iron
- (e) Inert gas
- (v) Radium
- (D)
- (a) IA (i) Liquid metal
- (1) Halogen
- (b) *d*-block (ii) Liquid non-metal (2)  $3s^2$   $3p^4$ elements
- (c) Mercury (iii) Diamond
- (3)  $ns^1$
- (d) Bromine (iv) VIA group
- (4) Variable valency

- (e) Carbon
  - (v) Alkali metals
- (5) Coinage metal
- (f) Sulphur (vi) Noble metal
- (6) Amalgam
- (g) Gold
- (vii) Transition
- (7) Hardest

metals

substance

(E) (a) A reactive non-metal; the atom has a large negative electron affinity

(i) Sodium

- (b) A soft metal; the atom has low
- (ii) Antimony
- ionisation energy (c) A metalloid that forms an oxide
  - (iii) Argon
- of the formula R<sub>2</sub>O<sub>3</sub> (d) A chemically unreactive gas
- (iv) Chlorine
- (F) (a) A reactive, pale yellow gas; the atom has a large negative electron
  - (i) Oxygen
  - affinity (b) A soft metal that reacts with
- (ii) Gallium
- water to produce hydrogen (c) A metal that forms an oxide of formula  $R_2O_3$
- (iii) Barium (iv) Fluorine
- (d) A colourless gas; the atom has moderately large negative electron affinity

### Answers

Answers: Subjective Type Questions

- 1. (a) Newland; (b) Moseley; (c) Atomic numbers of elements; (d) K, Ar; Co, Ni; Te, I; Pa, Th; (e) Li, Mg; Be, Al; B, Si; (f) Lanthanides and actinides; (g) Ten; (h) Sixth; (i) First; (j) one, i.e., 7th period; (k)  $(n-1)d^{1-10} ns^{1 \text{ or } 2}$ ; (l)  $(n-2)f^{1-14} (n-1)d^{0 \text{ or } 1} ns^2$ ; (m) Helium; (n) Chlorine; (o) Fluorine; (p) Cations; (q) eV/atom or kcal/mol or kJ/mol; (r) Isoelectronic; (s)Francium, mercury and bromine; (t) 4; (u) Out of 117 elements 94 metals and 23 non-metals; (v) I or IA (alkali group), zero group, 18 (inert or noble gases); (w) Bridge elements; (x) 28.
- 2. (i) I < Br < F < CI; (ii)  $Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$  [Isoelectronic ions]; (iii)  $Ca^{2+} < Ar < CI^- < S^{2-}$ ; (iv) Na < AI < Mg < Si; (v)  $Br^+ < Br < Br^-$ ; (vi)  $Pb^{4+} < Pb^{2+} < Pb$ ; (vii) HF < HCI < HBr < HI; (viii)  $I_2 < Br_2 < CI_2 < F_2$ ; (ix) Li < B < Be; (xi)  $SiO_2 < P_2O_5 < SO_3 < CI_2O_7$ ; (xii) I < Br < CI < F; (xiii) Cu < Zn < Na; (xiv) Na < AI < Fe < Pb; (xv) C < N < F < O.
- (a) Al; (b) Ar; (c) Sc; (d) Ne, Xe respectively; (e) IIIB; (f) IIA;
   (g) IA group, VIth period, (h) VIIA group, 2nd period; (i) VIA group (oxygen); (j) IA and IIA groups.
- (a) (i) s-block—12, 19, 38, (ii) p-block—17, 31, 54, (iii) d-block—25, 42, 23; (b) Mn, Fe, Cu; (c) Four blocks—(i) s-block, (ii) p-block, (iii) d-block, (iv) f-block; (d) (i) (A) Mg (B) Ne (C) N (D) Na (E) F (ii) D, (iii) E, (iv) D, (v) B.
- (a) (i) Cl, (ii) Cs, (iii) Al, (iv) F, (v) O, (vi) Xe, (vii) C, (viii) Li, (ix) Br.
  - (b) (i) Cl, (ii) Na, (iii) Ar, (iv) Cl; Ar, (v) Al, (vi) Cl, (vii) P, (viii) S.

- (c) (i) Ar, (ii) Cl, (iii) Cl, (iv) Ar, (v) Na.
- (d) (i) A < C < B, (ii) C < B < A, (iii) A < B < C, (iv) C < B < A.
- **6.** (a) K $-1s^2$ ,  $2s^22p^6$ ,  $3s^23p^6$ ,  $4s^1$ 
  - (b) Mn $-1s^2$ ,  $2s^22p^6$ ,  $3s^23p^63d^5$ ,  $4s^2$
  - (c) Cu $-1s^2$ ,  $2s^22p^6$ ,  $3s^23p^63d^{10}$ ,  $4s^1$
  - (d) Ce (Z = 58), Lu (Z = 71)
  - (e) Th (Z = 90), Lr (Z = 103)
- 7. (a) s-block = groups 1, 2
  p-block = groups 13 to 18
  d-block = groups 3 to 12
  - (b) For elements in a period, the number of energy shells is equal and for elements in the group, the number of electrons in the valence shell (outermost shell) is the same.
  - (c) groups 1, 2, 13-18
     (d) s-block : ns <sup>1-2</sup>; p-block : ns<sup>2</sup>np<sup>1-6</sup>
     d-block : (n 1)d<sup>1-10</sup>ns<sup>0-2</sup>;
     f-block : (n 2)f<sup>1-14</sup>(n 1)d<sup>0-1</sup>ns<sup>2</sup>
- 8. (a) Nuclear charge in Mg<sup>2+</sup> is more than O<sup>2-</sup>.
  - (b) N has stable configuration since it has half filled 2p-orbitals.
  - (c) O has much smaller size than S. The electron density is high in oxygen and thus, addition of electron is difficult.
  - (d) Alkali metal has the lowest and noble gas has the highest ionisation enthalpy in a period.
- 9. Ununennium; 2, 8, 18, 32, 32, 18, 8, 1; MCl; M2O.
- **10.** (a) Element 114 belongs to carbon family. Hence, the formula with fluorine will be  $AF_4$ , where A represents the element 114.
  - (b) Element 120 belongs to alkaline earth metal's family. Hence, its formula of the oxide will be MO, where M represents element 120.

## ILLUSTRATIONS OF OBJECTIVE QUESTIONS



- 1. What is the atomic number of last member of the seventh period of the extended form of periodic table?
  - (a) 116

(b) 118

(c) 120

(d) 122

Ans. (b)

[Hint: The last member of the sixth period is radon. Its atomic number is 86. In the seventh period energy shells 7s, 5f,

6d and 7p are completed, i.e., 2 + 14 + 10 + 6 = 32electrons are to be accommodated. Thus, in the 7th period, 32 elements will be present. So, the atomic number of the last member will be 86 + 32 = 118.

- 2. An element 'X' with atomic number 114 has recently been discovered. Its IUPAC name is:
  - (a) Eka-lead
- (b) Ununfortium
- (c) Ununquadium
- (d) Bohrium

Ans. (c)

[Hint: Un - un - quad - ium] 1

3. The process requiring absorption of energy is:

(a)  $F \longrightarrow F$ (c)  $Cl \longrightarrow Cl^-$  (b)  $H \longrightarrow H^-$ (d)  $O \longrightarrow O^{2-}$ 

Ans. (d)

[Hint: Second electron gain enthalpy is an endothermic process as the second electron is added to a negatively charged particle. Energy is needed to overcome force of repulsion.]

- Which transition involves maximum amount of energy?
  - (a)  $M^-(g) \longrightarrow M(g) + e$
  - (b)  $M^{-}(g) \longrightarrow M^{+}(g) + 2e$
  - (c)  $M^+(g) \longrightarrow M^{2+}(g) + e$
  - (d)  $M^{2+}(g) \longrightarrow M^{3+}(g) + e$

Ans. (d)

[Hint: 3rd I.P. > 2nd I.P. > 1st I.P.]

- 5. Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup> and Si<sup>4+</sup> are isoelectronic ions. Their ionic size follows the order:
  - (a)  $Na^+ < Mg^{2+} < Al^{3+} < Si^{4+}$
  - (b)  $Na^+ < Mg^{2+} < Al^{3+} > Si^{4+}$
  - (c)  $Na^+ < Mg^{2+} > Al^{3+} > Si^{4+}$
  - (d)  $Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$

Ans. (d)

[Hint:  $\frac{z}{e}$  Na<sup>+</sup> = 1.1, Mg<sup>2+</sup> = 1.2, Al<sup>3+</sup> = 1.3 and Si<sup>4+</sup> = 1.4 As  $\frac{Z}{\rho}$  increases, size decreases.]

- 6. (i) There are four *d*-block series.
  - (ii) Total d-block elements are 40.
  - (iii) Last d-block series starts with element actinium.
  - (iv) All members of d-block series are stable elements and found in nature.

The correct statements are:

- (a) (i), (ii) and (iii)
- (b) (i) and (iii)
- (c) (i) and (iv)
- (d) All

Ans. (a)

- 7. The formula of the binary compound formed by the element with atomic number 120 and sulphur is: (b) X<sub>2</sub>S (c) XS<sub>2</sub>
  - (a) XS

Ans. (a)

[Hint: The electronic configuration of the element X with atomic number 120 is [Uuo]  $8s^2$ . Thus, it belongs to second group and its valency is 2.]

- Elements A, B, C, D and E have the following electronic configurations:
  - (A)  $1s^2$ ,  $2s^2$   $2p^1$
- (B)  $1s^2$ ,  $2s^2 2p^6$ ,  $3s^2 3p^1$
- (C)  $1s^2$ ,  $2s^2 2p^6$ ,  $3s^2 3p^3$
- (D)  $1s^2$ ,  $2s^2 2p^6$ ,  $3s^2 3p^5$
- (E)  $1s^2$ ,  $2s^2 2p^6$ ,  $3s^2 3p^6$ ,  $4s^1$

The elements which belong to the same group of the periodic table are:

- (a) (A) and (C)
- (b) (A) and (B)
- (c) (A) and (D)
- (d) (A) and (E)

Ans. (b)

- 9. In the long form of periodic table, the number of period indicates the value of:
  - (a) atomic number
  - (b) atomic mass
  - (c) principal quantum number
  - (d) azimuthal quantum number

[Hint: The serial number of the period indicates the principal quantum number (n) which is the value of the valence shell of the atoms of the elements present in that period.]

- 10. Which one of the following statements is incorrect in relation to ionisation enthalpy?
  - (a) Ionisation enthalpy increases for each successive electron
  - (b) The greater increase in ionisation enthalpy is experienced on removal of electron from core noble gas configuration
  - (c) End of valence electrons is marked by a big jump in ionisation enthalpy
  - (d) Removal of electron from orbitals bearing lower n value is easier than from an orbital having higher n value

Ans. (d)

[Hint: Removal of electron from orbitals bearing lower value of n is difficult than from the orbital having higher value of

- 11. The correct order regarding electronegativity of hybrid orbitals of carbon is: IC.B.S.E. 2006]
  - (a)  $sp < sp^2 < sp^3$
- (b)  $sp < sp^2 > sp^3$
- (c)  $sp > sp^2 < sp^3$
- (d)  $sp > sp^2 > sp^3$

[Hint: Electronegativity increases as s-character in hybrid orbital increases.]

- 12. The electronic configurations of four elements are :
  - (i) [Xe] 6s<sup>1</sup>
- (ii) [Xe]  $4f^{14}5d^16s^2$
- (iii) [Ar]  $4s^24p^5$
- (iv) [Ar]  $3d^74s^2$

Which one of the following statements about these elements is not correct?

- (a) (i) is a strong reducing agent
- (b) (ii) is a d-block element
- (c) (iii) has high negative electron gain enthalpy
- (d) (iv) shows variable oxidation state

Ans. (b)

[Hint: (ii) is a last member of lanthanide series, i.e., 4f-element.]

- 13. Which of the following ions is most unlikely to exist?
  - (a) Li

(b) Be<sup>2+</sup>

(c) B-

(d) F

Ans. (a)

[Hint: Metals are electropositive, they do not form anion.]

- **14.** The element having very high ionization enthalpy but zero electron gain enthalpy is:
  - (a) H

(b) F

(c) He

(d) Be

Ans. (c)

[Hint: Inert gases have zero electron affinity.]

- 15. The second ionization energy is maximum for :
  - (a) boron
- (b) beryllium
- (c) magnesium
- (d) aluminium

Ans. (a)

**[Hint:**  $B_5 \longrightarrow 1s^2$ ,  $2s^2$ ,  $2p^1$ 

Second electron is to be removed from completely filled s-subshell, which is difficult.]

- **16.** The radii of F,  $F^-$ , O and  $O^{2-}$  are in the order :
  - $(a) O^{2-} > F^- > F > O$
- (b)  $F^- > O^{2-} > F > O$
- (c)  $O^{2-} > O > F^- > F$
- (d)  $O^{2-} > F^{-} > O > F$

Ans. (d)

[Hint: Anions are larger than neutral atoms. Oxygen is larger than fluorine as the nuclear charge is less.]

- 17. In the sixth period, the orbitals are filled as:
  - (a) 6s 5f 6d 6p
- (b) 6s 4f 5d 6p
- (c) 5s 5p 5d 6p
- (d) 6s 6p 6d 6f

Ans. (b)

- **18.** In the periodic table, which of the following trends is correct in a period ?
  - (a) Electron affinity decreases
  - (b) Electronegative character decreases
  - (c) Electropositive character increases
  - (d) Non-metallic nature increases

Ans. (d)

- **19.** The atomic radius of elements of the following series should be nearly the same :
  - (a) Na, K, Rb, Cs
- (b) Na, Mg, Al, Si
- (c) Fe, Co, Ni, Cu
- (d) F, Cl, Br, I

Ans. (c)

[Hint: Transition metals of the same series have nearly the same atomic radius.]

- **20.** In the following, the element with the highest ionisation energy is:
  - (a) [Ne]  $3s^2 3p^1$
- (b) [Ne]  $3s^2 3p^3$
- (c) [Ne]  $3s^2 3p^2$
- (d) [Ne]  $3s^2 3p^4$

Ans. (b)

**[Hint :** [Ne]  $3s^2$   $3p^3$  is a symmetrical configuration. Thus, this atom has extra stability.]



# **OBJECTIVE QUESTIONS**

			. · · ·	

### Set I: This set contains questions with single correct answer.

1.	The 'Law of triads' was enunciated by:	12.	The elements which occupy their positions in periodic ta	ıble
	(a) Mendeleev $\square$ (b) Newland $\square$	<u> </u>	just after the members of zero group are:	
	(c) Lother Meyer $\Box$ (d) Döbereiner $\Box$		(a) metals	
2.	The group number of an element in periodic table indicates:		(c) radioactive	
	(a) valency with respect to hydrogen	13.	An element having electronic configuration [Ar] 3d <sup>2</sup>	$4s^2$
	(b) the atomicity	!	belongs to:	
	(c) the number of electrons in the outermost shell $\Box$		(a) $d$ -block $\square$ (b) $f$ -block	
	(d) none of the above		(c) s-block	
3.	Which of the following statements is not correct about	14.	Elements belonging to same subgroup of periodic ta	able
	Lother Meyer's classification in the form of curve?		have generally the same:	
	(a) The elements present at the peaks are chemically very		(a) electronic configuration	
	active		(b) number of electrons in the outermost shell	
	(b) Alkaline earth metals are present at the descending		(c) chemical properties	
	portions of the curve $\Box$		(d) physical properties	
	(c) Halogens occupy ascending portions of the curve $\Box$	15.	The number of elements in fifth period of periodic table	e is:
	(d) The elements present in the troughs are chemically very		(a) 8	
	reactive and are known as representative elements $\square$		(c) 18	
4.	Which element was named Eka-aluminium by Mendeleev?	16.	An element which belongs to third period and fifth gre	oup
	(a) Scandium		has electronic configuration:	
	(c) Germanium $\Box$ (d) Indium $\Box$		(a) $1s^2$ , $2s^22p^6$ , $3s^2$ $3p^3$	
5.	Without looking at the periodic table, select the elements		(c) $1s^2$ , $2s^2 2p^6$ , $3s^2 3p^4 \square$ (d) none of these	
	of IIIA group of the periodic table (Atomic numbers are	17.	Which of the following is a d-block element?	
	given):		(a) Fr	
	(a) 3, 11, 19, 37		(c) Zn	
	(c) 7, 15, 31, 49	18.	d-block elements in long form of periodic table are place	ced:
6.	The transition elements have a characteristic electronic		(a) on the extreme left $\Box$ (b) on the extreme right	
	configuration which can be represented as:		(c) at the bottom $\Box$ (d) none of these	
	(a) $(n-2)s^2p^6d^{1-10}(n-1)s^2p^6ns^2$	19.	Ce (58) is a member of:	•
	(b) $(n-2)s^2p^6d^{1-10}(n-1)s^2p^6d^{1 \text{ or } 2} ns^1$		(a) s-block $\Box$ (b) $p$ -block	
	(c) $(n-1)s^2p^6d^{10} ns^2np^6nd^{1-10}$		(c) $d$ -block $\square$ (d) $f$ -block	
	(d) $(n-1)s^2p^6d^{1-10}ns^1$ or 2	20.	Which of the following is not an actinide?	
7.	The attempt for classifying elements by plotting the atomic		[D.P.M.T. 20	005]
•	masses of elements against the volumes was made by:		(a) Curium	
	(a) Döbereiner		(c) Uranium	
	(c) Lother Meyer	21.	Europium is: [D.P.M.T. 20	
8.	Who presented the law of octave?		(a) s-block $\Box$ (b) p-block	
	(a) Döbereiner		(c) $d$ -block $\square$ (d) $f$ -block	
	(c) Lother Meyer	22.	Variable valency is a general feature of:	
9.	How many elements were known when Mendeleev		(a) s-block elements	
	presented the periodic table?		(c) $d$ -block elements $\square$ (d) none of these	
	(a) 63	23.	Which one of the following ions is paramagnetic?	
	(c) 92		(a) $Ag^+$	
10.	The basis of periodic law presented by Mendeleev was:		(c) $K^+$	
	(a) valency	24.	Mark the group which has maximum number of elem-	ents
	(c) atomic number		in Mendeleev's periodic table:	-
11.	The modern Mendeleev's periodic table consists of		(a) I	
	groups:	-	(c) III	
	(a) seven	25.	Diagonal relationship in periodic table is shown	by
	(c) nine		elements of and periods :	A 14 4

	(a) I and II	l 37.	The halogens are:
	(c) III and IV	. 1:	(a) normal elements
26.	An element (X) which occurs in the second period has ar		(b) noble elements
	outer electronic configuration $s^2p^1$ -what is the formula and		(c) transition elements
	nature of its oxide?		(d) inner-transition elements
	(a) $XO_3$ , basic $\Box$ (b) $X_2O_3$ , acidic $\Box$	38.	^ ^ ·
	(c) $X_2O_3$ , basic $\Box$ (d) $XO_2$ , acidic $\Box$		ionic radii show: [C.B.S.E. (P.M.T.) 2003]
27.	An element of atomic mass 40 has 2, 8, 8, 2 as the electronic	:	(a) an increase from O <sup>2-</sup> to F <sup>-</sup> and then decrease from Na <sup>+</sup>
	configuration. Which one of the following statements	l l	to Al <sup>3+</sup>
	regarding this element is not correct?		(b) a decrease from O <sup>2-</sup> to F <sup>-</sup> and then increase from Na <sup>+</sup>
	(a) It forms an amphoteric oxide		to Al <sup>3+</sup>
	(b) It belongs to IIA group		(c) a significant increase from $O^{2-}$ to $Al^{3+}$
	(c) It belongs to IV period	1	(d) a significant decrease from $O^{2-}$ to $Al^{3+}$
	(d) It has 20 neutrons		Modern extended periodic table was given by:
28.	The most predominantly electrovalent compounds will be	1	(a) Bohr $\square$ (b) Lother Meyer $\square$
	obtained from the combination of elements belonging to		(c) Mosley
	(a) I and VII groups   (b) II and VI groups   (c)		In the modern periodic table, one of the following does not
	(c) III and V groups $\Box$ (d) none of these $\Box$		have appropriate position:
29.	Which one of the following configurations represents a		(a) inert gases
	metallic character?	'	(b) inner-transition elements
	(a) 2, 8, 2	ı	(c) transition elements
	(c) 2, 8, 7		(d) fluorine
30.	The first ionisation enthalpies of Na, Mg, Al and Si are in	l l	Which one of the following grouping represent a collection
	the order of:		of isoelectronic species? (At. numbers, $Cs = 55$ and $Br = 35$ )
	(a) Na $<$ Mg $>$ Al $<$ Si $\square$ (b) Na $>$ Mg $>$ Al $>$ Si $\square$	1	[A.I.E.E.E. 2003]
	(c) Na $<$ Mg $<$ Al $>$ Si $\square$ (d) Na $>$ Mg $>$ Al $<$ Si $\square$		(a) $N^{3-}$ , $F^{-}$ , $Na^{+}$
31.	Ionisation enthalpy of K would numerically the same as		(c) Be, $Al^{3+}$ , $Cl^{-}$
	(a) Electronegativity of K <sup>+</sup>	42.	The formation of $O_{(g)}^{2-}$ starting from $O_{(g)}$ is endothermic
	(b) Electron gain enthalpy of K <sup>+</sup>		by 639 kJ mol <sup>-1</sup> . If electron gain enthalpy of $O_{(g)}$ is -141 kJ
	(c) Electron gain enthalpy of Ar		mol <sup>-1</sup> , the second electron gain enthalpy of oxygen would
	(d) Ionisation enthalpy of Ca	.	be:
32.	The electronegativity of the following elements increases		(a) $-780 \text{ kJ mol}^{-1}$
	in the order of:		(c) + 498 kJ mol <sup>-1</sup> $\Box$ (d) - 498 kJ mol <sup>-1</sup> $\Box$
	(a) C, N, Si, P	ı	[ <b>Hint:</b> $O_{(g)} + 2e^{-} \longrightarrow O_{(g)}^{2-}$ ; $\Delta H = 639 \text{ kJ mol}^{-1}$ (i)
	(c) Si, P, C, N		$O_{(g)} + e^{-} \longrightarrow O_{(g)}^{-}$ ; $\Delta H = -141 \text{ kJ mol}^{-1}$ (ii)]
33.	The order in which the following oxides are arranged		Subtracting equation (ii) from equation (i)
	according to decreasing basic nature is:		$O_{(g)}^{-} + e^{-} \longrightarrow O_{(g)}^{2-}$ ; $\Delta H = 639 + 141 = 780 \text{ kJ mol}^{-1}$ ]
	(a) CuO, Na <sub>2</sub> O, MgO, Al <sub>2</sub> O <sub>3</sub>	43.	Which of the following elements has the maximum electron
	(b) Al <sub>2</sub> O <sub>3</sub> , MgO, CuO, Na <sub>2</sub> O		gain enthalpy?
	(c) MgO, Al <sub>2</sub> O <sub>3</sub> , CuO, Na <sub>2</sub> O		(a) oxygen
	(d) Na <sub>2</sub> O, MgO, Al <sub>2</sub> O <sub>3</sub> , CuO		(c) fluorine
34.	The difference between ions and atoms is of:	44.	The set representing the correct order of first ionisation
	(a) relative size	ı	enthalpy is: [I.I.T. (S) 2001] (a) $K > Na > Li$
	(c) presence of charge $\Box$ (d) all of these $\Box$		
35.	Na <sup>+</sup> is smaller than Na-atom because:		, ,
	(a) nucleus in each case contains different nucleons		If we go from Li to F in the second period, there would be a decrease in:
	(b) sodium atom has an electron lesser than sodium ion	'	
		.	· · ·
	(c) sodium atom has 11 electrons and sodium ion has 16	1	(c) ionisation enthalpy (d) electronegativity (17)
	electrons		The element having electronic configuration [Kr] $4d^{10}$ $4f^{14}$ , $5s^2$ $5p^6$ $5d^1$ , $6s^2$ belongs to:
	(d) the force of attraction is less in Na <sup>+</sup> than in Na-atom	'	
	than in ivaluation	ıİ	
36.	The highest valency of halogens with respect to oxygen is	- I	
	(a) 1		
	(c) 2		(a) Na < Be < B $\Box$ (b) F <sup>-</sup> < O <sup>2-</sup> < N <sup>3-</sup> $\Box$
	. , ,	İ	(c) Na < Li < K $\Box$ (d) Fe <sup>3+</sup> < Fe <sup>2+</sup> < Fe <sup>4+</sup> $\Box$

48.	In going from left to right in a period:			Lowest ionisation enthalpy in periods is shown by:
	(a) the basic nature of the oxides increases			(a) inert gases
	(b) acidic nature decreases			(c) alkali metals □ (d) alkaline earth metals □
•	(c) the basic nature of the oxides decreases		60.	Which of the following is basic?
	(d) no gradation in the nature of oxides is observed			(a) $F_2$ $\square$ (b) $Cl_2$ $\square$
49.	The elements with atomic numbers 58 to 71 are called:			(c) $Br_2$ $\Box$ (d) $I_2$ $\Box$
	(a) normal elements $\square$ (b) transition elements		61.	Strongest reducing agent among the following is:
	(c) lanthanides			(a) F
50.	An element R forms the highest oxide R <sub>2</sub> O <sub>5</sub> . R belongs	to:		(c) Br
	(a) IV group		62.	The elements with atomic numbers 10, 18, 36, 54 and 86 are
	(c) VI group			all:
51.	Transition metals are characterised by the properties exce			(a) light metals
0	(a) variable valency			(c) halogens
	(b) coloured compounds		63.	The elements on the right side of the periodic table are:
	(c) high melting and boiling points		00.	(a) non-metals
	(d) no tendency to form complexes			(c) transition elements $\Box$ (d) metalloids $\Box$
<b>E</b> 2	· -		6.1	
52.	Ionisation enthalpy in the alkali group:		04.	Which of the following atoms has the largest atomic radius?
	(a) increases from Li to Cs			(a) Cs
	(b) decreases from Li to Cs		<b>45</b>	(c) Pb
	(c) remains the same		65.	Which of the following is the weakest acid?
	(d) bears no gradation			(a) HF
53.	The ionisation enthalpy of isotopes of an element will			(c) HBr
	(a) same		66.	Electron affinity of :
	(b) different			(a) carbon is higher than oxygen
	(c) dependent on atomic masses			(b) sulphur is lesser than oxygen
	(d) dependent on the number of neutrons present in			(c) iodine is higher than bromine $\Box$
	nucleus			(d) chlorine is higher than fluorine
54.	The ionic radius of a cation is always:		67.	The correct order of relative stability of half filled and
	(a) less than atomic radius			completely filled shells is:
	(b) more than atomic radius			(a) $p^3 < d^5 < d^{10} < p^6$
	(c) equal to atomic radius			(c) $p^3 < d^{10} < d^5 < p^6$
	(d) cannot be predicted		68.	The electronic configuration of an element A is $1s^2$ , $2s^2$ $2p^5$ .
55.	The screening effect of 'd' electrons is:			The formula of substance containing only A will be:
	(a) much more than s-electrons			(a) $A \square$ (b) $A_2 \square$
	(b) equal to s-electrons			(c) $A_5$ $\square$ (d) $A_7$ $\square$
	(c) equal to p-electrons		69.	The electronic configuration of element A is $1s^2$ , $2s^2$ $2p^6$ ,
	(d) much less than s-electrons			$3s^2$ while of the element B is $1s^2$ , $2s^2$ $2p^5$ . The formula of
56.	Which of the following statements is incorrect?			the compound containing A and B will be:
	(a) Among all the elements, fluorine has the high	nest		(a) $AB$ $\square$ (b) $A_2B$ $\square$
	electron gain enthalpy		İ	(c) $AB_2$ $\square$ (d) $A_2B_6$ $\square$
	(b) Among all the elements, helium has the high	nest	70.	The valency shell of element A contains 3 electrons while
	ionisation enthalpy		İ .	the valency shell of element B contains 6 electrons. If A
	(c) Elements of groups 1, 2, 13, 14, 15, 16 and 17 are ca	lled		combines with B, the probable formula of the compound
	representative elements			formed will be:
	(d) All the <i>d</i> -block elements are metallic in nature			(a) $AB_2$ $\Box$ (b) $A_2B$ $\Box$
57.			1	(c) $A_2B_3$ $\square$ (d) $A_3B_2$ $\square$
	enthalpy?		71	Which one of the following has the highest melting point?
	(a) H		/1.	• • • • • • • • • • • • • • • • • • • •
	(c) He			(a) Na
50	The first ionisation enthalpies of four consecutive elements		72	
58.	<del>-</del> .		12.	Which one of the following is most acidic?
	present in the second period of the periodic table are		1	(a) Al <sub>2</sub> O <sub>3</sub>
	11.3, 14.5 and 13.6 eV respectively. Which one of	me	70	(c) MgO
	following is the first ionisation enthalpy of nitrogen?	1043	73.	Which of the following is an amphoteric oxide?
	[E,A,M,C,E,T, (Med.) 2	_		(a) MgO $\Box$ (b) Al <sub>2</sub> O <sub>3</sub> $\Box$ (c) SiO $\Box$ (d) PrO
	(a) 13.6			(c) $SiO_2$ $\Box$ (d) $P_2O_5$ $\Box$
	(c) 11.3		i	

74.	Which of the following is the correct statement?		ŧ.	In the series carbon, nitrogen, oxygen and fluorine, electron-
	(a) SO <sub>2</sub> is anhydride of sulphuric acid		1	egativity:
	(b) NO <sub>2</sub> is anhydride of nitric acid			(a) decreases from carbon to fluorine
	(c) Cl <sub>2</sub> O <sub>7</sub> is anhydride of perchloric acid .		1	(b) remains constant
	(d) P <sub>2</sub> O <sub>5</sub> is anhydride of orthophosphorus acid		4	(c) decreases from carbon to oxygen and then increases
75.	Which is the most acidic oxide?		1	(d) increases from carbon to fluorine
	(a) $Cl_2O$ $\square$ (b) $Cl_2O_3$		89.	Ionisation energy of nitrogen is more than oxygen because:
	(c) $Cl_2O_5$ $\Box$ (d) $Cl_2O_7$		1	(a) nucleus has more attraction for electrons
76.	Which of the following halides is not oxidised by MnO	$O_2$ ?	and the state of t	(b) half filled $p$ -orbitals are more stable $\square$
	(a) $F^-$		3	(c) nitrogen atom is small
	(c) Br		1	(d) more penetration effect
77.	Which of the following orders is correct for the rela	tive		Lanthanide contraction explains :
•	strength of the acids?			(a) density of the series
	(a) $HClO_4 > HNO_3 > H_2SO_4 > HCl$		1	(b) atomic volume of the series
	(b) $HCIO_4 > HC1 > HNO_3 > H_2SO_4$			(c) chemical activity of the series
•	(c) $HClO_4 > H_2SO_4 > HCl > HNO_3$		1	(d) size of the atoms of the series $\Box$
	(d) $HClO_4 > HNO_3 > H_2SO_4 > HCl$		91.	The outermost electronic configuration of the most electron-
78.	The most non-metallic element among the following i	s:		egative element is:
	(a) $1s^2$ , $2s^2$ $2p^6$			(a) $ns^2 np^3$
	(c) $1s^2$ , $2s^2$ $2p^4$		-	(c) $ns^2 np^5$
79.	The highest bond strength amongst the following, is of		92.	Amongst the following elements (whose electronic config-
, , , .	(a) HF			urations are given below) the one having highest ionisation
*	(c) HBr			energy is: [I.LT. 1990; .C.B.S.E.(P.M.T.) 2009]
80.	An element <i>M</i> has an atomic number 9 and atomic mass		Table and the same	(a) [Ne] $3s^2 3p^1$
	Its ion will be represented by:	, 17.		(c) [Ne] $3s^2 3p^2$
	(a) $M$ $\square$ (b) $M^{2+}$		93.	The electronic configuration of the element which is just
	(c) $M^ \square$ (d) $M^{2-}$			above the element with atomic number 43 in the same
81.				periodic group is:
٠.٠	(a) 92			(a) $1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^5$ , $4s^2$
	(c) 100			(b) $1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^5$
82.				(c) $1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^6$ , $4s^1$
Ű <b>.</b>	(a) angstrom units			(d) $1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^1$ $4p^6$
	(c) cm		94.	The statement that is not correct for the periodic classi-
83.			į	fication of elements is:
	According to law of triads the atomic mass of Na will	-	No. of Contract of	(a) The properties of elements are periodic functions of their
	(a) 23			atomic numbers
	(c) 46			(b) Non-metallic elements are lesser in number than
84.			er residence	metallic elements
	easily?			(c) The first ionisation energies of the elements along the
	(a) Li, Na, K			periods do not vary in a regular manner with the
	(c) O, S, Se		0	increase in atomic number
85.		by:		(d) For transition elements the d-subshells are filled with
	(a) alkali metals	Ó	1	electrons monotonically with increase in atomic
	(b) inert gases			number 🗆
	(c) representative elements		95.	If the atomic number of an element is 33, it will be placed
	(d) halogens		sh na na da	in the periodic table in the:
86.			Thomas Spanis	(a) first group
	group of the periodic table. They are called:		THE PERSON NAMED IN COLUMN NAM	(c) fifth group $\Box$ (d) seventh group $\Box$
	(a) alkaline earth metals □ (b) inert gases		96.	Which one of the following ions has the smallest radius?
	(c) alkali metals		i i	(a) $C^{4-}$
87.		ents	-	(c) $K^+$ $\Box$ (d) $Ca^{2+}$ $\Box$
	most electropositive element?		97.	The most electropositive element is:
	(a) [He] $2s^1$			(a) Cs
	(c) [Xe] $6s^1$	П		(c) Li

	Among the following, the element which is not liquid at	112.	Chloride of an element 'A' gives neutral solution in water.
	room temperature (30°C) is:		In the periodic table, the element 'A' belongs to:
	(a) Ga		(a) first group
	(c) Cs $\square$ (d) Br $\square$	112	(c) fifth group
99.	Which of the block of elements does belong to inert gases?	115.	of elements in the periodic table?
	(a) s-block $\Box$ (b) p-block $\Box$		(a) Lanthanum
	(c) $d$ -block $\square$ (d) $f$ -block $\square$	1	(c) Chromium
100.	Which of the following elements has the lowest ionisation	114.	An element of atomic number 29 belongs to:
	enthalpy?		(a) s-block $\Box$ (b) p-block $\Box$
	(a) Na	1	(c) $d$ -block $\Box$ (d) $f$ -block $\Box$
	(c) Mg	115.	A trend common to both groups 1 and 17 elements in the
101.	Which one of the following is smallest in size?		periodic table as atomic number increases is:
	(a) $Na^+$ $\square$ (b) $O^{2-}$ $\square$		(a) increase in oxidising nature
	(c) $N^{3-}$ $\square$ (d) $F^{-}$ $\square$	ł	(b) increase in atomic radius
102.	Which of the following has the lowest ionisation enthalpy?		(c) increase in maximum valency $\Box$
	(a) $4s^1$ $\Box$ (b) $3d^2$ $\Box$		(d) increase in reactivity with water $\Box$
	(c) $3p^6$ $\Box$ (d) $2p^6$ $\Box$	116.	Which of the following has largest radius?
103	Of the following elements, which one has the highest		(a) $O^{2-}$ $\square$ (b) $Mg^{2+}$ $\square$
100.	electronegativity?		(c) $Na^+$ $\square$ (d) $F^ \square$
	(a) I	117.	Which one is the correct order of the size of the iodine
	(c) C1		species?
104	Which of the following is the smallest cation?		(a) $I > I^+ > I^-$
101.	(a) $Na^+$		(c) $I^+ > I^- > I$
	(c) $Ca^{2+}$ $\Box$ (d) $Al^{3+}$ $\Box$	118.	Which of the following configurations represents atoms of
105			element having a large difference between first and the
105.	Among the following outermost configurations of transition metals which shows the highest oxidation state, is:		second ionisation energy?
			(a) $1s^2$ , $2s^2 2p^4$
	5 2		(c) $1s^2$ , $2s^22p^6$ , $3s^1$
106		119.	In which of the following arrangements, the order is not
100.	Which of the following ions has the lowest magnetic		according to the property indicated against it?
	moment? (a) $Cu^{2+}$ $\Box$ (b) $Ni^{2+}$ $\Box$		[A.I.E.E.E. 2005]
	2.		(a) $Al^{3+} < Mg^{2+} < Na^{+} < F$ increasing ionic size $\Box$
1.05			(b) $B < C < N < O$ increasing first ionisation enthalpy $\Box$
107.	Modern periodic table is based on the atomic number of		(c) I < Br < F < Cl increasing electron gain enthalpy
	the elements. The experiment which proved the significance	1	(with negative sign)
	of the atomic number was:		(d) Li < Na < K < Rb increasing metallic radius □
	(a) Millikan's oil drop experiment	120.	. A sudden large jump between the values of second and third
	(b) Moseley's work on X-ray spectra		ionisation energies of an element would be associated with
	(c) Bragg's work on X-ray diffraction	1	the electronic configuration:
400	(d) Discovery of X-rays by Rontgen		(a) $1s^2$ , $2s^2$ $2p^6$ , $3s^1$
108.	Which of the following pairs has both members from the		(c) $1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^2$ $\Box$ (d) $1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $\Box$
	same group of the periodic table?	121.	. In the long form of the periodic table, all the non-metals
	(a) Na, Ca		are placed with:
	(c) Ca, Cl		(a) s-block $\Box$ (b) p-block $\Box$
109.	Which of the following set of ions represents a collection	Ì	(c) $d$ -block $\square$ (d) $f$ -block $\square$
	of isoelectronic species? [A.I.E.E. 2006]	122.	. The lanthanide contraction is responsible for the fact that :
	(a) $Ba^{2+}$ , $Sr^{2+}$ , $K^+$ , $Ca^{2+}$ $\Box$ (b) $K^+$ , $Cl^-$ , $Ca^{2+}$ , $Sc^{3+}$ $\Box$	1	[A.I.E.E.E. 2005]
	(c) $N^{3-}$ , $O^{2-}$ , $F^{-}$ , $S^{2-}$ $\square$ (d) $Li^{+}$ , $Na^{+}$ , $Mg^{2+}$ , $Ca^{2+}$ $\square$		(a) Zr and Y have about the same radius
110.	Aluminium is diagonally related to:		(b) $Zr$ and $Nb$ have similar oxidation state
	(a) Li		(c) $Zr$ and $Hf$ have about the same radius
	(c) Be		(d) Zr and Zn have the same oxidation state
111.	In the sixth period of the extended form of periodic table,	123	. Of cobalt and zinc salts, which are attracted in magnetic
	the orbitals are filled as:		field?
	(a) $6s$ , $5f$ , $6d$ , $6p$		(a) Cobalt salts
	(c) be by 6d bf $\square$ (d) be 4f 5d by $\square$	1	(c) Both

124.	The electronic configuration of an element is $1s^2$ , $2s^3 3p^3$ . What is the atomic number of the element which below the above element in the periodic table?		<ul> <li>(b) The second ionisation potential of Mg is greater than the second ionisation potential of Na □</li> <li>(c) The first ionisation potential of Na is less than the first</li> </ul>
	(a) 34		ionisation potential of Mg
	(c) 33		(d) The third ionisation potential of Mg is greater than third
125.	Element X belongs to 4th period. It contains 18	and 1	ionisation potential of Al
	electrons in the penultimate and ultimate orbit.	The X	138. Element with atomic number 56 belongs to which block?
	should be:		[A.F.M.C. 2002]
	(a) normal element $\Box$ (b) transition element		(a) $s$ $\Box$ (b) $p$ $\Box$
	(c) inert gas		(c) $d$ $\Box$ (d) $f$
	(d) inner-transition element		139. Which of the following orders is wrong? [C.B.S.E. 2002]
126.	Electron gain enthalpy of X would be equal to:		(a) $NH_3 < PH_3 < AsH_3 - Acidic$
	(a) electron affinity of X		(b) Li $<$ Be $<$ B $<$ C $-$ IE <sub>1</sub>
	(b) ionisation potential of X <sup>-</sup>		(c) $Al_2O_3 < MgO < Na_2O < K_2O - Basic$
	(c) ionisation potential of X		(d) $\operatorname{Li}^+ < \operatorname{Na}^+ < \operatorname{K}^+ < \operatorname{Cs}^+$ – Ionic radius
	(d) none of the above		140. Which is true about electronegativity order of the following
127.	Element with atomic number 35 belongs to:		elements? [B.V. (Pune) 2002]
	(a) 3rd period		(a) $P > Si$ $\square$ (b) $C > N$
	(c) 5th period		(c) $C > Br$ $\Box$ (d) $Sr > Ca$
128.	Most of the man-made synthetic elements occur:		141. Eka-aluminium and Eka-silicon are known as:
	(a) in actinide series $\Box$ (b) in lanthanide series		[M.E.E.(Kerala) 2002]
	(c) in coinage metals	. 🗆	(a) gallium and germanium
	(d) in alkaline earth metals		(b) aluminium and silicon
129.	Which is the largest stable atom?	_	(c) iron and sulphur
	(a) V		(d) proton and silicon
400	(c) Al		142. Two elements whose electronegativities are 1.2 and 3.0, the
130.	Which of the following is strongest base?	_	bond formed between them would be: [P.E.T.(M.P.) 2002]
	(a) $Be(OH)_2$		(a) ionic
101	(c) Al(OH) <sub>3</sub>		. (c) coordinate $\Box$ (d) metallic $\Box$
131.	Which has largest atomic size?		143. Chloride ion and potassium ion are isoelectronic. Then:
	(a) Al		[K.C.E.T. 2002]
	(c) $Al^{3+}$ $\Box$ (d) $Al^{+}$		(a) their sizes are same
132.	Alkaline earth metals form ions of the formula:	_	(b) Cl <sup>-</sup> ion is bigger than K <sup>+</sup> ion
	(a) $M^+$		(c) K <sup>+</sup> ion is relatively bigger
100	(c) $M^{2+}$		(d) their sizes depend on other cation and anion
133.	Which one of these is basic?		144. Identify the least stable ion amongst the following:
	(a) $CO_2$		[I.I.T.(S) 2002]
104	(c) NO <sub>2</sub>		(a) Li
134.	Of cobalt and zinc salts, which are attracted in a ma	agnetic	(c) B <sup>-</sup>
	field?	_	145. Increasing order of electron gain enthalpy is:
	(a) Cobalt salts		[P.E.T.(Raj.) 2003]
105	(c) Both (a) and (b) (d) None		(a) $N < O < Cl < Al$
133.	Which of the following species has the highest electro	on gạin	(c) $Al < N < O < Cl$
	enthalpy? (a) F⁻ □ (b) O	_	146. Which of the following sets is of coinage metals?
	(a) F		[D.P.M.T. 2003]
136	Among the isoelectronic species, K <sup>+</sup> , S <sup>2-</sup> , Cl <sup>-</sup> and C		(a) Cu, Ag, Hg
150.	radii of the ions decrease as:	a uic	(c) Au, Ag, Zn
	(a) $Ca^{2+} > K^+ > C\Gamma > S^{2-}$		147. According to modern periodic law, variations in the
	(a) $Ca^{-} \times K^{-} \times C1^{-} \times S2^{-} \times K^{+} \times Ca^{2+}$		properties of elements is related to their: [A.I.E.E.E. 2003]
			(a) atomic weights $\square$ (b) nuclear weights $\square$
	(c) $S^2 > C\Gamma > K^+ > Ca^{2+}$		(c) atomic numbers □ (d) neutron-proton ratios □
105	(d) $K^+ > Ca^{2+} > S^{2-} > C\Gamma$		148. Which of the following has maximum ionisation enthalpy?
13/.	The incorrect statement among the following is:	h a <i>fi</i>	[P.M.T. (Pb.) 2003]
	(a) The first ionisation potential of Al is less than the ionisation potential of Ma		
	ionisation potential of Mg		

	· · · · · · · · · · · · · · · · · · ·	
	(a) K	158. Which of the following has lowest ionisation energy?
	(c) Mg	[C.P.M.T. 2007]
149.	The electronic configuration of transition elements is	(a) Oxygen □ (b) Nitrogen □
	exhibited by: [P.M.T. (Pb.) 2003]	(c) Fluorine $\Box$ (d) Sulphur $\Box$
	(a) $ns^1$	159. The electronic configuration of the element with maximum
	(c) $ns^2 (n-1)d^{10}$	electron affinity is: [P.E.T. (Kerala) 2008]
150.	General electronic configuration of outermost and penulti-	(a) $1s^2$ , $2s^2$ $2p^3$
	mate shell is $(n-1) s^2 (n-1) p^6 (n-1) d^x n s^2$ . If $n=4$ and	(a) $1s^2$ , $2s^2$ $2p^3$
	x = 5, then number of protons in the nucleus will be:	(e) $1s^2$ , $2s^2$ $2p^6$ , $3s^1$
	[P.E.T. (M.P.) 2003]	160. The first ionisation energy of oxygen is less than that of
	(a) > 25 $\Box$ (b) < 24 $\Box$	nitrogen. Which of the following is the correct reason for
	(c) 25	this observation? [P.E.T. (Kerala) 2008]
151.	Increasing order of density is: [P.E.T. (M.P.) 2003]	(a) Lesser effective nuclear charge of oxygen than nitrogen
	(a) Li $<$ K $<$ Na $<$ Rb $<$ Cs	
	(b) Li $<$ Na $<$ K $<$ Rb $<$ Cs	(b) Lesser atomic size of oxygen than nitrogen □
	(c) $Cs < Rb < K < Na < Li$	(c) Greater inter-electron repulsion between two electrons
	(d) $K < Li < Na < Rb < Cs$	in the same p- orbital counter balances the increase in
152.	Outer electronic configurations of K, Cu and Cr are	effective nuclear charge on moving from nitrogen to
	respectively: [B.H.U. 2003]	oxygen □
	(a) $4s^1$ , $3d^{10}$ $3d^5$ $\Box$ (b) $4s^2$ , $3d^{10}$ $3d^4$ $\Box$	(d) Greater effective nuclear charge of oxygen than nitrogen
	(c) $4s^1$ , $3d^9$ $3d^4$	
153.	Identify the correct order of the size of the following:	(e) Higher electronegativity of oxygen than nitrogen
	[C.B.S.E. 2007, 10]	161. Column I Column II
•	(a) $Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$	(A) He (i) High electron gain enthalpy (B) C1 (ii) Most electropositive element
	(b) Ar $<$ Ca <sup>2+</sup> $<$ K <sup>+</sup> $<$ Cl <sup>-</sup> $<$ S <sup>2-</sup>	(C) Ca (iii) Strongest reducing agent
	(c) $Ca^{2+} < Ar < K^+ < Cl^- < S^{2-}$	(D) Li (iv) Highest ionisation energy
	(d) $Ca^{2+} < K^+ < Ar < S^{2-} < C\Gamma$	The correct match of contents in Column I with those in
154.	With which of the following electronic configuration an	Column II is: [P.E.T. (Kerala) 2008]
	atom has the lowest ionisation enthalpy? [C.B.S.E. 2007]	(a) A—(iii), B—(i), C—(ii), D—(iv)
	(a) $1s^2 2s^2 2p^3$	(b) A—(iv), B—(iii), C—(ii), D—(i)
	(c) $1s^2 2s^2 2p^6$	(c) A—(ii), B—(iv), C—(i), D—(iii)
155.	In which one of the following pairs the radius of the second	(d) A—(i), B—(ii), C—(iii), D—(iv)
	species is greater than that of the first? [P.E.T. (Kerala) 2007]	(e) A—(iv), B—(i), C—(ii), D—(iii)
	(a) Na, Mg $\Box$ (b) $O^{2-}$ , $N^{3-}$ $\Box$	162. An element X belongs to fourth period and fifteenth group
	(c) $\operatorname{Li}^+$ , $\operatorname{Be}^{2+}$ $\square$ (d) $\operatorname{Ba}^{2+}$ , $\operatorname{Sr}^{2+}$ $\square$	of the periodic table. Which one of the following is true
	(e) Al, Be □	regarding the outer electronic configuration of X? It has: [P.M.T. (Kerala) 2008]
156.	The electronic configurations of four elements are given	(a) partially filled <i>d</i> -orbitals and completely filled <i>s</i> -orbital
	below. Arrange these elements in the correct order of the	
	magnitude (without sign) of their electron affinity.	(b) completely filled s-orbital and completely filled
	(i) $2s^2 2p^5$ (ii) $3s^2 3p^5$	p-orbitals
	(iii) $2s^2 2p^4$ (iv) $3s^2 3p^4$	(c) completely filled s-orbital and half filled p-orbitals $\square$
	Select the correct answer using the codes given below:	(d) half filled d-orbitals and completely filled s-orbital $\square$
	[P.M.T. (Kerala) 2007]	(e) completely filled $s$ -, $p$ - and $d$ -orbitals
	(a) (i) $<$ (ii) $<$ (iii) $<$ (iv) $\square$ (b) (ii) $<$ (i) $<$ (iv) $<$ (iii) $\square$	163. The correct order of increasing electron affinity of halogens
	(c) (i) $<$ (iii) $<$ (iv) $<$ (ii) $\square$ (d) (iii) $<$ (iv) $<$ (ii) $<$ (i) $\square$	is: [P.E.T. (M.P.) 2008]
	(e) (iii) $<$ (iv) $<$ (i) $<$ (ii) $\square$	(a) $F < Cl < Br < I$
157	The electronic configuration of the atom having maximum	(c) $I < Br < Cl < F$
	difference in first and second ionisation energies is:	164. In which of the following arrangements, the sequence is not
	[P.M.T. (Kerala) 2007]	strictly according to the property written against it?
	(a) $1s^2$ , $2s^2$ $2p^6$ , $3s^1$	[A.I.E.E.E. 2009] (a) $CO_2 < SiO_2 < SnO_2 < PbO_2$ : increasing oxidising power $\square$
	(c) $1s^2$ , $2s^2$ $2p^1$	(a) $CO_2 < SIO_2 < SIO_2 < FIO_2$ . Increasing oxidising power $\Box$ (b) HF < HCl < HBr < HI : increasing acid strength
	(e) $1s^2$ , $2s^2 2p^3$	(b) III \ IICI \ IIII \ III . IIICIeasing acid suengin

(c) $NH_3 < PH_3 < AsH_3 < SbH_3$ : increasing basic stre (d) $B < C < O < N$ : increasing first ionisation en	-	(a) Cl < F < O < S
165. The set representing the correct order of ionic ra	dius is:	171. In a periodic table, the basic character of oxides:
	E.E. 2009]	[J.E.E. (W.B.) 2010]
(a) $Li^+ > Be^{2+} > Na^+ > Mg^{2+}$		(a) increases from left to right and decreases from top to
(b) $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$	<u> </u>	bottom
(c) $\text{Li}^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{Be}^{2+}$		(b) decreases from right to left and increases from top to
(d) $Mg^{2+} > Be^{2+} > Li^+ > Na^+$		bottom LI
166. The correct order of ionisation energy of C, N, C [C.E.T. (Karnatz	3	(c) decreases from left to right and increases from top to bottom
(a) $F < N < C < O$ $\Box$ (b) $C < N < O < F$	aka) 2009]	(d) decreases from right to left and decreases from top to
(c) $C < O < N < F$		bottom
167. Ionisation energy of He <sup>+</sup> is $19.6 \times 10^{-18}$ J atom <sup>-1</sup> . T	3	172. Which of the following orders regarding ionization energy
of the first stationary state $(n = 1)$ of $Li^{2+}$ is:		is correct? [J.E.E. (W.B.) 2010]
·	.E.E. 2010]	(a) $N > O > F$
(a) $8.82 \times 10^{-17} \text{ J atom}^{-1} \square$ (b) $4.41 \times 10^{-16} \text{ J a}$	tom <sup>-1</sup>	(c) $N > O < F$
(c) $-4.41 \times 10^{-17} \text{ J atom}^{-1} \square$ (d) $-2.2 \times 10^{-15} \text{ J a}$	tom <sup>-1</sup>	173. The diagonal partner of element B is :[J.E.E. (Orissa) 2010]
[Hint: $E_H$ (for H) $\times$ $Z^2$ = I.E.		(a) Li
$E_{\rm H} \times 4 = 1.E. \text{ of He}^+ = -19.6 \times 10^{-1}$	<sup>18</sup> J	(c) Si $\Box$ (d) Mg $\Box$
or $E_{H} = -\frac{19.6 \times 10^{-18}}{4} J$		174. The first $(\Delta_i H_1)$ and second $(\Delta_i H_2)$ ionisation enthalpies
*	***	(in kJ mol <sup>-1</sup> ) and the electron gain enthalpy $(\Delta_{eg}H)$ in
$E_{Li^{2+}} = E_H \times 9 = -\frac{19.6 \times 10^{-18}}{4} \times 9$	-	kJ mol $^{-1}$ of elements I, II, III, IV and V are given below :
$= -44.1 \times 10^{-18} \text{ J} = -4.41 \times 10^{-18} \text{ J}$	10-17 1 1	Element $\Delta_{i}H_{1}$ $\Delta_{i}H_{2}$ $\Delta_{eg}H$
168. The correct sequence which shows decreasing or		I 520 7300 - 60
	.E.E. 2010]	II 419 3051 -48
(a) $O^{2-} > F^{-} > Na^{+} > Mg^{2+} > Al^{3+}$		III 1681 3374 –328
(b) $Al^{3+} > Mg^{2+} > Na^{+} > F^{-} > O^{2-}$		IV 1008 1846 - 295 V 2372 5251 + 48
(c) $Na^+ > Mg^{2+} > Al^{3+} > O^{2-} > F$		
(c) $Na^+ > Mg^{2+} > Al^{3+} > O^{2-} > F^-$		The most reactive metal and least reactive non-metal of
(c) $Na^{+} > Mg^{2+} > Al^{3+} > O^{2-} > F^{-}$ (d) $Na^{+} > F^{-} > Mg^{2+} > O^{2-} > Al^{3+}$ [Hint: The ionic radii decreases in isoelectronic species		The most reactive metal and least reactive non-metal of these are respectively: [P.E.T. (Kerala) 2010]
<ul> <li>(c) Na<sup>+</sup> &gt; Mg<sup>2+</sup> &gt; Al<sup>3+</sup> &gt; O<sup>2-</sup> &gt; F</li> <li>(d) Na<sup>+</sup> &gt; F<sup>-</sup> &gt; Mg<sup>2+</sup> &gt; O<sup>2-</sup> &gt; Al<sup>3+</sup></li> <li>[Hint: The ionic radii decreases in isoelectronic specie number increases i.e., z/e increases.</li> </ul>	es as atomic	The most reactive metal and least reactive non-metal of these are respectively: [P.E.T. (Kerala) 2010]  (a) I and V
(c) $Na^+ > Mg^{2+} > Al^{3+} > O^{2-} > F^-$ (d) $Na^+ > F^- > Mg^{2+} > O^{2-} > Al^{3+}$ [Hint: The ionic radii decreases in isoelectronic species number increases i.e., $z/e$ increases. Ions $O^{2-}$ $F^ Na^+$ $Mg^{2+}$	es as atomic  Al <sup>3+</sup>	The most reactive metal and least reactive non-metal of these are respectively:  (a) I and V  (b) V and II  (c) II and V  (d) IV and V
<ul> <li>(c) Na<sup>+</sup> &gt; Mg<sup>2+</sup> &gt; Al<sup>3+</sup> &gt; O<sup>2-</sup> &gt; F</li> <li>(d) Na<sup>+</sup> &gt; F<sup>-</sup> &gt; Mg<sup>2+</sup> &gt; O<sup>2-</sup> &gt; Al<sup>3+</sup></li> <li>[Hint: The ionic radii decreases in isoelectronic specie number increases i.e., z/e increases.</li> </ul>	es as atomic  Al <sup>3+</sup>	The most reactive metal and least reactive non-metal of these are respectively: [P.E.T. (Kerala) 2010]  (a) I and V
(c) Na <sup>+</sup> > Mg <sup>2+</sup> > Al <sup>3+</sup> > O <sup>2-</sup> > F  (d) Na <sup>+</sup> > F <sup>-</sup> > Mg <sup>2+</sup> > O <sup>2-</sup> > Al <sup>3+</sup> [Hint: The ionic radii decreases in isoelectronic specie number increases <i>i.e.</i> , $z/e$ increases.  Ions O <sup>2-</sup> F <sup>-</sup> Na <sup>+</sup> Mg <sup>2+</sup> $z/e$ $\frac{8}{10} = 0.8$ $\frac{9}{10} = 0.9$ $\frac{11}{10} = 1.1$ $\frac{12}{10} = 1.2$	es as atomic $Al^{3+}$ $\frac{13}{10} = 1.3$	The most reactive metal and least reactive non-metal of these are respectively:  (a) I and V  (b) V and II  (c) II and V  [Hint: The values suggest that I is Li, II is K, III is Br, IV is I and V is He.]  175. The electron affinity values of elements A, B, C and D are
(c) $Na^+ > Mg^{2+} > Al^{3+} > O^{2-} > F^-$ (d) $Na^+ > F^- > Mg^{2+} > O^{2-} > Al^{3+}$ [Hint: The ionic radii decreases in isoelectronic species number increases i.e., $z/e$ increases. Ions $O^{2-}$ $F^ Na^+$ $Mg^{2+}$	as as atomic $Al^{3+}$ $\frac{13}{10} = 1.3 l$ increasing	The most reactive metal and least reactive non-metal of these are respectively:  (a) I and V  (b) V and II  (c) II and V  (d) IV and V  [Hint: The values suggest that I is Li, II is K, III is Br, IV is I and V is He.]  175. The electron affinity values of elements A, B, C and D are respectively -135, -60, -200 and -348 kJ mol <sup>-1</sup> . The outer
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(c) Na <sup>+</sup> > Mg <sup>2+</sup> > Al <sup>3+</sup> > O <sup>2-</sup> > F  (d) Na <sup>+</sup> > F <sup>-</sup> > Mg <sup>2+</sup> > O <sup>2-</sup> > Al <sup>3+</sup> [Hint: The ionic radii decreases in isoelectronic species number increases i.e., z/e increases.  Ions O <sup>2-</sup> F <sup>-</sup> Na <sup>+</sup> Mg <sup>2+</sup> z/e 8/10 = 0.8 9/10 = 0.9 11/10 = 1.1 12/10 = 1.2  169. Among the elements Ca, Mg, P, Cl, the order of atomic radii is:   IC.B.S.E. (P.M. (a) Mg < Ca < Cl < P □ (b) Cl < P < Mg < (c) P < Cl < Ca < Mg □ (d) Ca < Mg < P < 170. Which of the following represents the correct	es as atomic $Al^{3+}$ $\frac{13}{10} = 1.3$ increasing  (A.T.) 2010  Ca   Cl   crofer of	The most reactive metal and least reactive non-metal of these are respectively:  (a) I and V  (b) V and II  (c) II and V  (d) IV and V  [Hint: The values suggest that I is Li, II is K, III is Br, IV is I and V is He.]  175. The electron affinity values of elements A, B, C and D are respectively -135, -60, -200 and -348 kJ mol <sup>-1</sup> . The outer electronic configuration of B is: [E.A.M.C.E.T. (Engg.) 2010]
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(c) Na <sup>+</sup> > Mg <sup>2+</sup> > Al <sup>3+</sup> > O <sup>2-</sup> > F  (d) Na <sup>+</sup> > F <sup>-</sup> > Mg <sup>2+</sup> > O <sup>2-</sup> > Al <sup>3+</sup> [Hint: The ionic radii decreases in isoelectronic species number increases i.e., z/e increases.  Ions O <sup>2-</sup> F <sup>-</sup> Na <sup>+</sup> Mg <sup>2+</sup> z/e 8/10 = 0.8 9/10 = 0.9 11/10 = 1.1 12/10 = 1.2  169. Among the elements Ca, Mg, P, Cl, the order of atomic radii is:   IC.B.S.E. (P.N. (a) Mg < Ca < Cl < P □ (b) Cl < P < Mg < (c) P < Cl < Ca < Mg □ (d) Ca < Mg < P < 170. Which of the following represents the correct increasing electron gain enthalpy with negative	as as atomic $Al^{3+}$ $\frac{13}{10} = 1.3 l$ increasing  A.T.) 2010]  Ca	The most reactive metal and least reactive non-metal of these are respectively:  (a) I and V
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(c) Na <sup>+</sup> > Mg <sup>2+</sup> > Al <sup>3+</sup> > O <sup>2-</sup> > F  (d) Na <sup>+</sup> > F <sup>-</sup> > Mg <sup>2+</sup> > O <sup>2-</sup> > Al <sup>3+</sup> [Hint: The ionic radii decreases in isoelectronic species number increases i.e., z/e increases.  Ions O <sup>2-</sup> F <sup>-</sup> Na <sup>+</sup> Mg <sup>2+</sup> z/e 8/10 = 0.8 9/10 = 0.9 11/10 = 1.1 12/10 = 1.2  169. Among the elements Ca, Mg, P, Cl, the order of atomic radii is: IC.B.S.E. (P.M. (a) Mg < Ca < Cl < P □ (b) Cl < P < Mg < (c) P < Cl < Ca < Mg □ (d) Ca < Mg < P <  170. Which of the following represents the correct increasing electron gain enthalpy with negative IC.B.S.E. (P.M. Set II: This set contains questions with the set of the following cases:  (a) a smaller cation (b) a larger anion (c) large charges on cation and anion (d) a cation without noble gas configuration  176. Stability of ions of Ge, Sn and Pb will be in the	as as atomic  Al <sup>3+</sup> 13/10 = 1.3 l increasing  A.T.) 2010l Ca	The most reactive metal and least reactive non-metal of these are respectively:  (a) I and V
(c) Na <sup>+</sup> > Mg <sup>2+</sup> > Al <sup>3+</sup> > O <sup>2-</sup> > F  (d) Na <sup>+</sup> > F <sup>-</sup> > Mg <sup>2+</sup> > O <sup>2-</sup> > Al <sup>3+</sup> [Hint: The ionic radii decreases in isoelectronic species number increases i.e., z/e increases.  Ions O <sup>2-</sup> F <sup>-</sup> Na <sup>+</sup> Mg <sup>2+</sup> z/e 8/10 = 0.8 9/10 = 0.9 11/10 = 1.1 12/10 = 1.2  169. Among the elements Ca, Mg, P, Cl, the order of atomic radii is: IC.B.S.E. (P.M. (a) Mg < Ca < Cl < P □ (b) Cl < P < Mg < (c) P < Cl < Ca < Mg □ (d) Ca < Mg < P <  170. Which of the following represents the correct increasing electron gain enthalpy with negative IC.B.S.E. (P.M. Set II: This set contains questions with the set of larger anion (b) a larger anion (c) large charges on cation and anion (d) a cation without noble gas configuration  176. Stability of ions of Ge, Sn and Pb will be in the (a) Ge <sup>2+</sup> < Sn <sup>2+</sup> < Pb <sup>2+</sup> □ (b) Ge <sup>4+</sup> > Sn <sup>4+</sup> > I	as as atomic  Al <sup>3+</sup> 13/10 = 1.3 l increasing  A.T.) 2010l Ca	The most reactive metal and least reactive non-metal of these are respectively:  (a) I and V
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A.	(a) Na		(b) Br <sub>2</sub>	್ಟ∎್ರ	186.	Which of the following el	leme	nts belongs to halogen gr	roup?
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	(c) Hg	Π,	(d) Ga			(a) $1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^5$			
182.	Which of the following is	/are	the correct order of mo	bility?		(b) $1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ , 4	$1s^2$		
	(a) $Li^+ < Na^+ < K^+$		(b) $Na^+ < Mg^{2+} < Al^{3+}$			(c) [Ar] $3a^{10}$ , $4s^2$ $4p^5$			
	(c) $Al^{3+} < Mg^{2+} < Na^{+}$		(d) $Li^+ > Na^+ > K^+$		187.	Which of the following r	epre	sents the same element?	
183.	Stability order of +3 and	+1 s	tates of boron family e	lement		(a) 105		(b) Unnilpentium	
	is:					(c) Ha		(d) Rf	
	(a) $Ga^{3+} < In^{3+} < Tl^{3+}$		(b) $Ga^+ > In^+ > TI^+$		188.	Ionic radius of:		I.I.T.	1999]
	(c) $Ga^+ < In^+ < TI^+$					(a) $Ti^{4+} < Mn^{7+}$		(b) $^{35}Cl^- < ^{37}Cl^-$	
184.	Which of the following p	airs	contain elements with	similar		(c) $K^+ > Cl^-$		(d) $P^{3+} > P^{5+}$	
	atomic radii?				189.	Select the process/es whi	ich is	/are endothermic in nati	ure?
	(a) Co, Ni		(b) Zn, Mo			(a) $H + e^- \longrightarrow H^-$		(b) $O^- + e^- \longrightarrow O^{2-}$	
	(c) Rh, Ir		(d) Hf, Ti			(c) $Ar + e^- \longrightarrow Ar^-$		(d) $M \longrightarrow M^+ + e^-$	
185.	Which of the following	g sp	ecies has same num	ber of	190.	Choose the pair in which	ı IE <sub>1</sub>	of the first element is gr	reater
	unpaired electrons?			:		than IE <sub>1</sub> of second eleme	ent b	ut in case of IE2. The or	der is
	(a) Cr <sup>3+</sup>		(b) Mn <sup>2+</sup>			reversed :		· -	
	(c) Fe <sup>3+</sup>		(d) Cu <sup>2+</sup>	. 🗆		(a) N,O		(b) F, O	
						(c) Be, B		(d) P,S	

Ansu	iers =								
1. (d)	2. (c)	3. (d)	<b>4.</b> (b)	5. (d)	6. (d)	7. (c)	8. (b)	9. (a)	<b>10.</b> (b)
<b>11</b> . (c)	<b>12.</b> (d)	13. (a)	<b>14</b> . (b)	<b>15.</b> (c)	<b>16.</b> (a)	<b>17.</b> (c)	18. (d)	<b>19.</b> (d)	<b>20.</b> (d)
<b>21</b> . (d)	<b>22.</b> (c)	23. (b)	24. (c)	25. (b)	26. (b)	27. (a)	<b>28.</b> (a)	<b>29</b> . (a)	30. (a)
<b>31.</b> (b)	<b>32.</b> (c)	33. (d)	34. (d)	35. (c)	36. (d)	37. (a)	38. (d)	39. (d)	<b>40.</b> (b)
<b>41.</b> (a)	<b>42.</b> (b)	<b>43.</b> (b)	<b>44.</b> (b)	<b>45.</b> (b)	<b>46.</b> (d)	<b>47.</b> (b)	<b>48.</b> (c)	<b>49.</b> (c)	<b>50.</b> (b)
<b>51.</b> (d)	<b>52.</b> (b)	53. (a)	54. (a)	55. (d)	56. (a)	57. (d)	<b>58.</b> (b)	<b>59.</b> (c)	<b>60.</b> (d)
<b>61</b> . (d)	<b>62.</b> (b)	63. (a)	<b>64.</b> (a)	65. (a)	66. (d)	67. (d)	68. (b)	69. (c)	<b>70</b> . (c)
<b>71.</b> (d)	<b>72.</b> (a)	73. (b)	<b>74.</b> (c)	75. (d)	76. (a)	77. (b)	<b>78.</b> (b)	<b>79.</b> (a)	<b>80.</b> (c)
<b>81.</b> (b)	<b>82.</b> (a)	83. (a)	<b>84.</b> (a)	85. (b)	86. (d)	<b>87.</b> (c)	88. (d)	<b>89.</b> (b)	<b>90.</b> (d)
<b>91</b> . (c)	<b>92</b> . (b)	93. (a)	94. (d)	<b>95</b> . (c)	<b>96.</b> (d)	97. (a)	<b>98.</b> (b)	<b>99.</b> (b)	100. (b)
101. (a)	102. (a)	103. (d)	<b>104.</b> (d)	<b>105.</b> (c)	106. (a)	<b>107.</b> (b)	108. (d)	109. (b)	110. (c)
111. (d)	112. (a)	113. (d)	<b>114</b> . (c)	<b>115.</b> (b)	<b>116.</b> (a)	117. (d)	118. (c)	119. (b)	120. (d)
<b>121.</b> (b)	122. (c)	123. (a)	<b>124</b> . (c)	125. (b)	<b>126.</b> (b)	127. (d)	128. (a)	129. (d)	130. (b)
131. (a)	132. (c)	133. (b)	134. (a)	135. (b)	136. (c)	137. (b)	138. (a)	139. (b)	140. (a)
141. (a)	142. (a)	143. (b)	144. (b)	145. (c)	146. (a)	<b>147.</b> (c)	148. (d)	149. (d)	<b>150.</b> (c)
<b>151.</b> (a)	<b>152.</b> (a)	153. (a)	154. (b)	155. (b)	156. (e)	157. (a)	158. (d)	<b>159.</b> (c)	160. (c)
<b>161.</b> (e)	<b>162.</b> (c)	163. (b)	164. (c)	165. (b)	166. (c)	167. (c)	168. (a)	169. (b)	<b>170.</b> (b)
171. (c)	172. (c)	173. (c)	174. (c)	175. (c)	176. (a,b,c,d)	177. (a,b,c,d)	178. (a,b,c)	<b>179</b> . (a,b,c,d	) <b>180</b> . (b,c,d)
181. (b,c,d)	182. (a, c)	183. (c, d)	184. (a, c)	185. (b,c)	<b>186.</b> (a,c,d)	187. (a,b,c)	188. (b,d)	<b>189.</b> (b,c,d)	190. (a,c,d)



### **Objective Questions for IIT ASPIRANTS**



1. The paramagnetic species among the following is:

- (c) Cu<sup>+</sup>
- (d)  $Fe^{3+}$
- [Hint: Paramagnetic species have at least one unpaired electron. Write the electronic configuration and observe the unpaired orbital.
  - $Na^+: 1s^2, 2s^2 2p^6$

- $Zn^{2+}$ :  $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^2$   $3p^6$   $3d^{10}$  All paired;
- $Cu^+: 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$  All paired;
- $Fe^{3+}: 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5$  Unpaired orbitals]
- 2. The diamagnetic species among the following is:

- (b) Cd<sup>2+</sup>
- (c) Cr<sup>3+</sup>
- [Hint: Diamagnetic species have all paired electrons.
- $Cu^{2+}: 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^9$  Unpaired orbital;
- $Cr^{3+}: 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3$  Unpaired orbitals;
- $Co^{3+}: 1s^2, 2s^2 2p^6, 3s^2 3p^6 \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow$  Unpaired orbitals;
- $Cd^{2+}: 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}$  All paired ]
- The correct decreasing order of electropositive character among the following elements is:

- (a) Fe > Sc > Rb > Br > Te > F > Ca
- (b) Ca > Rb > Sc > Fe > Te > F > Br
- (c) Rb > Ca > Sc > Fe > Br > Te > F
- (d) Rb > Ca > Sc > Fe > Te > Br > F

[Hint: Remember the following points:

- (i) Alkali and alkaline earth metals are most electropositive. Alkali metals are more electropositive than alkaline earth metals.
- (ii) In d-block series, the elements near alkaline earth metals are more electropositive than rest of the
- (iii) Metalloids are less electropositive than metals.
- (iv) Halogens (Non-metals) are least electropositive. In halogen group, electropositive character increases as atomic number increases.]
- 4. The correct decreasing order of atomic size among the following species is:

- (a)  $Ca^{2+} > K^+ > Ar > Cl^- > S^{2-}$  (b)  $K^+ > Ca^{2+} > Cl^- > Ar > S^{2-}$
- (c)  $S^{2-} > CI^{-} > Ar > K^{+} > Ca^{2+}$  (d)  $S^{2-} > Ar > CI^{-} > Ca^{2+} > K^{+}$
- [Hint : In isoelectronic ions, the atomic size decreases as  $\frac{z}{a}$  ratio

$$S^{2-}\frac{z}{e} = \frac{16}{18}$$
;  $CI^{-}\frac{z}{e} = \frac{17}{18}$ ;  $Ar\frac{z}{e} = \frac{18}{18}$ ;  $K^{+}\frac{z}{e} = \frac{19}{18}$ ;  $Ca^{2+}\frac{z}{e} = \frac{20}{18}$ 

- 5. If each orbital can take maximum of three electrons, the number of elements in the third period of the periodic table will be:
  - (a) 12

(b) 6 .

(c) 8

(d) 24

[Hint: In third period, 3s- and 3p-orbitals are filled. Total orbitals to be filled = one s + three p = 4. Thus, number of elements  $=4\times3$  =12.]

- The number of elements which can be accommodated in the present set-up of the long form of the periodic table is:
  - (a) 120

(b) 118

(c) 122

(d) 124

[Hint: In the present set-up, on the basis of aufbau principle and four blocks of elements, the last period, i.e., 7th period is to accommodate 32 elements  $(7s^2, 5f^{14}, 6d^{10}, 7p^6)$ . Thus, total elements can be accommodated 118 (86 up to 6th period plus 32 in the 7th period).]

- 7. What would be the atomic number of the next halogen if discovered in future?
  - (a) 115

(b) 119

(c) 117

(d) 121

[Hint: The next halogen will have  $7s^27p^5$  outer configuration. Since, the filling of 7p-orbitals will begin after 5f- and 6dorbitals, thus the atomic number of the new halogen will be 112 (up to the filling of 6d-orbitals) plus 5, i.e., 117.]

The energies of the electron in a hydrogen like ion are given

 $E_n = -(2.18 \times 10^{-18}) Z^2 \left(\frac{1}{n^2}\right)$ , where *n* is principal quantum number and Z is the atomic number of the element. The ionisation energy (in kJ mol<sup>-1</sup>) of the Li<sup>2+</sup> ion is:

- (a)  $1.18 \times 10^3$
- (b)  $118 \times 10^3$
- (c)  $0.118 \times 10^3$
- (d)  $11.8 \times 10^3$

[Hint: Ionisation energy =  $(2.18 \times 10^{-18}) Z^2 \left(\frac{1}{n^2}\right) \times N \text{ J mol}^{-1}$  where

N is the Avogadro number.

For 
$$Li^{2+} = (2.18 \times 10^{-18}) \times 3^2 (1) \times 6.02 \times 10^{23} \text{J mol}^{-1}$$

First and second ionisation energies of magnesium are 7.646 and 15.035 eV respectively. The amount of energy in kJ needed to convert all the atoms of magnesium into Mg<sup>2+</sup> ions present in 12 mg of magnesium vapours is :

[Given :  $1eV = 96.5 \text{ k} \text{[ mol}^{-1} \text{]}$ 

(a) 1.1

(c) 2.0

(d) 0.5

[Hint: Total energy needed to convert one Mg atom into Mg2+ (gas) ion =  $IE_{II} + IE_{II}$ 

$$= 22.681 \text{ eV} = 2188.6 \text{ kJ mol}^{-1}$$

12 mg of Mg =  $0.5 \times 10^{-3}$  mole]

- 10. Which of the following has highest electron gain enthalpy?
  - (A) [Ne]  $3s^2 3p^3$ ;
- (B) [Ne]  $3s^2 3p^4$
- (C) [Ne]  $3s^2 3p^5$ ;
- (D) [Ne]  $3s^2 3v^2$
- (a) (A)
- (b) (B)
- (c) (C)
- (d) (D)

[Hint: The element (C) will have highest electron gain enthalpy as it easily gains one more electron to achieve stable configuration of next inert gas.]

- 11. The element with atomic number 35 belongs to :
  - (a) d-block

(b) f-block

(c) p-block

(d) s-block

[Hint: Write the electronic configuration on the basis of aufbau

$$1s^2$$
,  $2s^2 2p^6$ ,  $3s^2 3p^6 3d^{10}$ ,  $4s^2 4p^5$ 

The last electron is accommodated on p-energy shell. ]

- 12. The electronic configurations for some neutral atoms are given below:
  - (A)  $1s^2$ ,  $2s^2 2p^6$ ,  $3s^2$

(B)  $1s^2$ ,  $2s^2 2p^6$ ,  $3s^1$ 

(C)  $1s^2$ ,  $2s^2 2p^6$ ,  $3s^2 3p^2$ 

(D)  $1s^2$ ,  $2s^2 2p^6$ ,  $3s^2 3p^3$ 

Which of these is expected to have the highest second ionisation enthalpy?

(a) (A)

(b) (B)

(c) (C)

(d) (D)

[Hint: B atom after losing outermost electron acquires noble gas configuration (stable configuration). It is difficult to remove the next electron from B+ (1s2, 2s2 2p6) ion.]

- The amount of energy released when 106 atoms of iodine in vapour state are converted to I<sup>-</sup> ions is  $4.9 \times 10^{-13}$  J. What is the electron affinity of iodine in eV per atom?

- (b) 2.5
- (c) 2.75;

[Hint: Amount of energy released for 1 mole of iodine

$$=\frac{4.9\times10^{-13}}{10^6}\times6.02\times10^{23}$$

 $= 29.5 \times 10^4 \text{ J} = 295 \text{ kJ mol}^{-1}$ 

 $1 \text{ eV per atom} = 96.3 \text{ kJ mol}^{-1}$ 

List I

14. Match the following lists and select the correct answer:

(A)	$1s^2$ , $2s^2$	$2p^6$ , $3s^2$	$3p^6, 4s^1$	(1)	d-block element
<b>(B)</b> .	$1s^2$ , $2s^2$	$2p^6, 3s^2$ 3	$3p^6$	(2)	Halogen
(C)	$1s^2$ , $2s^2$	2p <sup>6</sup> , 3s <sup>2</sup> 3	3p <sup>6</sup> 3d <sup>6</sup> , 4s <sup>2</sup>	(3)	Alkali metal
(D)	$1s^2$ , $2s^2$	$2p^{5}$		(4)	Noble gas
	Α	В	С	D	
(a)	1	2	3	4	
(b)	3	4	1	2	
(c)	1	3	2	4	
(d)	2	4	3	1	

- 15. Which of the following is the wrong statement?
  - (a) All the actinide elements are radioactive
  - (b) Alkali and alkaline earth metals are s-block elements
  - (c) Chalcogens and halogens are p-block elements
  - (d) The first member of the lanthanide series is lanthanum
- Which of the following is the correct statement?
  - (a) The second ionisation potential of an atom is always less than the first ionisation potential.
  - (b) The addition of an electron to a neutral atom is an endothermic process
  - (c) Fluorine has the maximum electronegativity

- (d) The size of the cation is always less than the size of the neutral atom
- 17. (A), (B) and (C) are elements in the third short period. Oxide of (A) is ionic, that of (B) is amphoteric and of (C) a giant molecule. (A), (B) and (C) have atomic number in the order:
  - (a) (A) < (B) < (C)
- (b) (C) < (B) < (A)
- (c) (A) < (C) < (B)
- (d) (B) < (A) < (C)

**[Hint:**  $A_c$  B and C are magnesium, aluminium and silicon. Magnesium forms ionic oxide, MgO, aluminium forms amphoteric oxide, Al<sub>2</sub>O<sub>3</sub> and silicon forms a giant molecule, SiO2.]

18. Match the List I with List II and select the correct answer:

### List I

List II

- (A) Most electronegative element
- (1) Chlorine
- (B) The element having highest electron gain enthalpy
- (2) Hydrogen
- (C) Most abundant element in the universe
- (3) Nitrogen (4) Fluorine
- (D) Most abundant gas in atmosphere В C
- 2 3 (a) 4
- 2 3 (b) 4
- (c) 4 1 2 3
- (d)
- The five successive ionisation energies of the element are 800, 2427, 3658, 25024 and 32824 kJ mol<sup>-1</sup> respectively. The number of valence electrons is:
  - (a) 3
- (b) 5

[Hint: Fourth ionisation energy abruptly increases. This shows that fourth electron is removed from inert gas core.]

- Which of the following species has the negative electron gain enthalpy?
  - (a) F<sup>-</sup>

(b) O

(c) O

(d) Na<sup>+</sup>

[Hint: Energy is released when electron is added to O but energy is absorbed in rest of the cases when electron is added.]

- 21. The ionic radius of Cr is minimum in which of the following compounds?
  - (a) CrF<sub>3</sub>
- (b) CrCl<sub>3</sub>
- (c)  $Cr_2O_3$
- (d)  $K_2CrO_4$

[Hint: Cr has maximum oxidation number (+6) in K2CrO4 and thus, has minimum ionic radius.]

- 22. Arrange Ce<sup>3+</sup>, La<sup>3+</sup>, Pm<sup>3+</sup> and Yb<sup>3+</sup> in increasing order of their size:
  - (a)  $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
  - (b)  $Ce^{3+} < Yb^{3+} < Pm^{3+} < La^{3+}$
  - (c)  $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$ (d)  $Pm^{3+} < La^{3+} < Ce^{3+} < Yb^{3+}$

[Hint: Lanthanide contraction is observed in these ions, i.e., ionic radius decreases as atomic number increases.]

- 23. Which of the following statements related to the modern periodic table is incorrect?
  - (a) The p-block has 6 vertical columns, i.e., groups
  - (b) The *d*-block has 8 vertical columns

- (c) Each block contains a number of columns equal to the number of electrons that can occupy that subshell
- (d) The block indicates value of azimuthal quantum number (1) for the last subshell that received electrons in building up the electronic configuration.

[Hint: d-block has 10 columns.]

- 24. Following statements regarding the periodic trends of chemical reactivity of the alkali metals and the halogens are given. Which of these statements gives the correct picture?
  - (a) The reactivity decreases in the alkali metals but increases in halogens with increase in atomic number down the group
  - (b) In both the groups, the chemical reactivity decreases with increase in atomic number down the group
  - (c) In both the groups, the chemical reactivity increases with increase in atomic number down the group

- (d) In alkali group, the chemical reactivity increases but decreases in the halogens with increase in atomic number down the group
- 25. The values of electronegativity of atoms A and B are 1.20 and 4.0 respectively. The percentage ionic character of A - B bond is:
  - (a) 50.0%

(b) 72.2%

(c) 55.3%

(d) 43.0%

[Hint: % ionic character =  $16(4 - 1.2) + 3.5(4 - 1.2)^2 = 72.2$ ] The element with atomic number 118 (Uuo) has been discovered recently. Which of the following is not expected

for this element?

- (a) It is radioactive and unstable element
- (b) It is a solid at room temperature
- (c) Its ionisation enthalpy is minimum in the group
- (d) It has  $7s^27p^6$  outer shell configuration

### Auswers

									***	
1.	(d)	2. (b)	3. (d)	<b>4.</b> (c)	5. (a)	6. (b)	7. (c)	8. (d)	9. (a)	<b>10.</b> (c)
11.	(c)	<b>12.</b> (b)	13. (d)	14. (b)	<b>15</b> . (d)	<b>16.</b> (c)	17. (a)	<b>18.</b> (c)	<b>19.</b> (a)	<b>20.</b> (b)
21.	(d)	22. (a)	23. (b)	24. (d)	<b>25.</b> (b)	<b>26.</b> (b)				

## Matrix Matching Questions for IIT Aspirants

1. Match List-I with List-II:

List-I (Group/Period)\* List-II

(Element)

- (a) 7th period
- (p) Transition elements
- (b) IIIB group
- (q) Inner transition elements
- (c) IA
- (r) Hydrogen
- (d) VIIA
- (s) Halogens
- 2. Match List-I with List-II:

List-I
--------

List-II

- (a) (P + 1) > N
- (p) Al
- (b) (P + 1) = 7
- (q) Pb
- (c) (P + 1) < N
- (r) C
- (d) (P + 1) = N
- (s) Si

Here, P = Number of period.

N = Number of valence electrons.

[Hint:In p-block:

(P + 1) > N; (P + 1) < N, (P + 1) = N

respectively represent metal, non-metal and metalloid.

3. Match the atomic number in List-I, with the block in List-II and groups in List-III:

List-I	List-II	List-III
(Atomic number)	(Block)	(Group)*
·(a) 55	(p) p	(u) VIII
(b) 45	(q) f	(v) IIIB

<sup>\*</sup>Modern Mendeleev's Periodic Table

- (c) 81 (d) 64
- (r) s (s) d
- (w) IIIA (x) IA

4. Match List-I with List-II:

### List-I

List-II

- (a) Halogen
- (p) Oxygen
- (b) Chalcogen
- (g) Chlorine
- (c) Noble gas

- (r) Sulphur
- (d) Representative element (s) Neon
- 5. Match List-I with List-II:

### List-I

List-II (Information)

- (Element) (a) Rutherfordium
- (p) Z = 104
- (b) Kurchatovium
- (q) f-block
- (c) Thorium
- (r) d-block
- (d) Neptunium

- (s) Transuranic element
- 6. Match List-I with List-II:

#### List-I

(a) Döbereiner

List-II (p) Law of octave

- (b) Alexander Newlands
- (q) Davy Medal
- (c) A.E.B. de Chancourtois
- (r) Law of triads
- (d) Dmitri Mendeleev
- (s) Based on atomic weights

		-
7.	Match List-I with List-II:	ng pinadan vita igtir niggi kila
	List-I	List-II
	(a) Lanthanide contracti	on (p) d-block
	(b) Diagonal relationshi	p (q) Elements of 3rd period
	(c) Typical elements	(r) f-block
	(d) Inner transition elen	nents (s) Be–Al
8.	Match the electronic co	nfiguration (List-I) with the ioni-
	sation energy (List-II):	•
	List-I	List-II
	(Electronic	(Ionisation energy)
	configuration)	kJ/mol
	(2)2	(m) 2100

	the second secon	A second	l and Column-III:
Co	lumn-I	Column-II	Column-III
(Atomi	c number)	(Group)*	Column-III (Period)
(a) 13		(p) IIIA	(u) 6
(b) 35		(q) VIIA	(v) 5
(c) 56		(r) IIA	(w)3
(d) 78		(s) VIII	(x) 4
. Match t	he elements in	List-I with th	neir properties in Lis
. ]	List-I	List-Il	

List-I	List-II	
(Electronic	(Ionisation energy)	
configuration)	kJ/mol	
(a) $ns^2$	(p) 2100	
(b) $ns^2np^1$	(q) 1400	
(c) $ns^2np^3$	(r) 800	
(d) $ns^2np^6$	(s) 900	

(u) 70	, (S) VI	u (x/ 4
Match the elem	ents in List-I with	h their properties in List-II:
List-I	Lis	t-II
(a) Mercury	(p)	Metal
(b) Bromine	· (q)	Densest element
(c) Osmium	(r)	Element with highest melting point
(d) Wolfram (7	Tungsten) (s)	Liquid at room temp

Answ	ers =							
1. (a-p, q) 2. (a-p, q) 3. (a-r-x) 4. (a-q) 5. (a-p, r, s)	(b-p, q) (b-q) (b-q-r) (b-p, r) (b-p, r, s)	(c-r) (c-r) (c-p-w) (c-s) (c-q)	(d-r, s) (d-s) (d-q-v) (d-p, q, r) (d-q, s)	6. (a-r, s) 7. (a-p, r) 8. (a-s) 9. (a-p-w) 10. (a-p, s)	(b-p, q, s) (b-s) (b-r) (b-q-x) (b-s)	(c-s) (c-q) (c-q) (c-r-u) (c-p, q)	(d-s) (d-r) (d-p) (d-s-u) (d-p, r)	

10.

## **Assertion-Reason Type Questions**

The questions given below consist of an Assertion (A) and Reason (R). Use the following key to choose the correct answer.

- (a) If both (A) and (R) are correct and (R) is the correct explanation of the (A).
- (b) If both (A) and (R) are correct and (R) is not the correct explanation of (A).
- (c) If (A) is correct and (R) is incorrect.
- (d) If both (A) and (R) are incorrect.
- 1. (A) Each d-block series contains ten elements.
  - (R) The maximum capacity of *d*-orbitals is of ten electrons as in each series *d*-orbitals are gradually filled up.
- 2. (A) Helium and beryllium have similar outer electronic configuration  $ns^2$ .
  - (R) Both are chemically inert.

IA.LI.M.S. 199

- **3.** (A) Electron gain enthalpy of oxygen is less than that of fluorine but greater than that of nitrogen.
  - (R) Ionisation enthalpy is as follows:

N > O > F

[A.I.I.M.S. 1998]

- 4. (A) The first ionisation energy of Be is greater than that of B.
  - (R) 2p-orbital is lower in energy than 2s-orbital. [I.I.T. 2001]

- 5. (A) Cu<sup>2+</sup> is diamagnetic.
  - (R) All the orbitals present in Cu<sup>2+</sup> ion are doubly occupied.
- 6. (A) The size decreases as  $Pb > Pb^{2+} > Pb^{4+}$ .
  - (R)  $\frac{z}{e}$  increases, *i.e.*, force of attraction towards nucleus increases.
- **7.** (A) There are fourteen elements in the lanthanide series and fourteen elements in the actinide series.
  - (R) All the elements of the actinide series are radioactive.
- **8.** (A) The group 18 consists of elements which are in gaseous state under ordinary atmospheric conditions.
  - (R) All the elements of group 18 have stable configuration.
- 9. (A) First ionisation energy of nitrogen is lower than oxygen.
  - (R) Across a period effective nuclear charge decreases.

[A.I.I.M.S. 2005]

- 10. (A) F atom has a less negative electron affinity than chlorine.
  - (R) Additional electrons are repelled more effectively by 3*p* electrons in Cl atom than by 2*p* electrons in F atom.
- 11. (A) The ionic size of Mg<sup>2+</sup> is larger than Al<sup>3+</sup>.
  - (R) In isoelectronic species, greater the nuclear charge, less is the size.

	4										
Aus	were =										
						*				,	
1. (a)	2. (c)	3. (c)	<b>4.</b> (a)	5. (d)	6. (a)	7. (b)	8. (b)	9. (d)	<b>10</b> . (c)	11. (a)	
÷ (c)	(C)	O. (c)	(44)	J. (4)	٠; (۵)	(0)	- · · · · · ·	3. (4)	20. (0)	<b>11.</b> (4)	

<sup>\*</sup>Modern Mendeleev's Periodic Table

# THOUGHT TYPE QUESTIONS

### **THOUGHT 1**

Numerous forms of the periodic table have been devised from time to time. A modern version, which is most convenient and widely used is the long or extended form of periodic table. The aufbau principle and the electronic configuration of atoms provide a theoretical foundation for the periodic classification. The horizontal rows are called periods. There are altogether seven periods. The first period consists of 2 elements. The subsequent periods consist of 8, 8, 18, 18 and 32 elements respectively. The seventh period is incomplete and like the sixth period would have maximum of 32 elements.

Elements having similar outer electronic configurations in their atoms are grouped in vertical columns. These are referred to as groups or families. According to the recommendation of IUPAC, the groups are numbered 1 to 18 replacing the older notation of groups 0, IA, IIA, ......... VIIA, VIII, IB, ......... VII B.

Each successive period in the periodic table is associated with the filling up next higher principal energy level following aufbau sequence. The number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled. All the elements are classified into four blocks, *i.e.*, *s*-block, *p*-block, *d*-block and *f*-block depending on the type of atomic orbitals that are being filled with electrons.

1. An element belongs to group 17. It is present in third period and its atomic number is 17. What is the atomic number of the element belonging to same group and present in fifth period?

(a) 25

(b) 33

(c) 35

(d) 53

- **2.** Elements in the same vertical group of the periodic table have generally the same :
  - (a) atomic number
  - (b) electronic configuration
  - (c) atomic mass
  - (d) number of electrons in the outermost shell of their atoms
- 3. The element with atomic number 118 is likely to have the same outer shell configuration as the element with atomic number:

(a) 18

(b) 28

(c) 58

(d) 88

- **4.** What is the position of the element in the periodic **table** satisfying the electronic configuration (n-1)  $d^1$   $ns^2$  for n=4?
  - (a) 3rd period and 3rd group
  - (b) 4th period and 3rd group

- (c) 3rd period and 2nd group
- (d) 4th period and 2nd group
- 5. Elements A, B, C, D and E have the following electronic configurations:

(A)  $1s^2$ ,  $2s^2$   $2p^1$ 

(B)  $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^2$   $3p^1$ 

(C)  $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^2$   $3p^3$ 

(D)  $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^2$   $3p^5$ 

(E)  $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^2$   $3p^6$ 

Which among these will belong to same group in the periodic table ?

(a) (A) and (C)

(b) (A) and (D)

(c) (A) and (B)

(d) (A) and (E)

6. The outer electronic configuration of an element is,  $(n-2) f^7 (n-1) d^1 ns^2$ .

To which block in the long form of the periodic table does this belong?

(a) s-block

(b) p-block

(c) d-block

(d) f-block

7. The elements with atomic numbers 90 to 103 are known as:

(a) d-block elements

(b) lanthanides

(c) actinides

(d) transition elements

8. In Mendeleev's periodic table, silver belongs to IB group. The group to which silver belongs in long form of periodic table is:

(a) first

(b) eleventh

(c) tenth

(d) sixteenth

**9.** The elements in which 4f-orbitals are progressively filled are called as:

(a) lanthanides

(b) actinides

(c) transition elements

(d) chalcogens

10. If aufbau rule is not followed, Ca-20 will be placed in .....block.

(a) s-

(b) p-

(c) d-

(d) f-

[Hint: If aufbau rule is not followed, the electronic configuration of Ca-20 will be  $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^2$   $3p^6$   $3d^2$ , i.e., last electron will be accommodated on d- orbital.]

## THOUGHT 2

The minimum amount of energy required to remove the most loosely bound electron from an isolated atom in the gaseous state is known as ionisation energy or first ionisation energy or ionisation enthalpy ( $IE_1$ ) of the element. The energy required to remove the second electron from the monovalent cation is called second ionisation enthalpy ( $IE_2$ ). Similarly, we have third, fourth ......... ionisation enthalpies. The values of ionisation energy depends on a number of factors such as (i) size of the atom (ii) screening effect (iii) nuclear charge (iv) half filled and fully filled orbitals (v) shape of orbital.

In a group, the ionisation energy decreases from top to bottom. In a period, the value of ionisation energy increases from left to right with breaks where atoms have somewhat stable configurations.

- 1. Compared to the second ionisation energy ( $IE_2$ ) of an atom, the third ionisation energy  $(IE_3)$  is:
  - (a) the same
- (b) greater
- (c) smaller
- (d) half
- 2. In a period, the ionisation energy is lowest for the:
  - (a) noble gases
- (b) halogens
- (c) alkaline earth metals
- (d) alkali metals
- 3. The electronic configurations of some neutral elements are
  - (A)  $1s^2$ ,  $2s^2$ ; (B)  $1s^2$ ,  $2s^2 2p^1$ ; (C)  $1s^2$ ,  $2s^2 2p^4$ ; (D)  $1s^2$ ,  $2s^2 2p^3$ which of these electronic configurations would be expected to have highest second ionisation energy  $(IE_2)$ ?
  - (a) (A)

(b) (B)

- (c) (C)
- (d) (D)
- The first (IE<sub>1</sub>) and second (IE<sub>2</sub>) ionisation energies (kJmol<sup>-1</sup>) of a few elements are shown below:

	$IE_1$	IE <sub>2</sub>
(A)	2372	5251
(B)	520	7300
(C)	900	1760
(D)	1680	3380
Which	of the above	e elements is likely to be a noble gas?
(a) (A	)	(b) (B)

- (c) (C) (d) (D) 5. In question no. 4, which of the element is likely to be a
  - non-metal?
- (b) (B)

(a) (A) (c) (C)

- (d) (D)
- 6. Which of the order for ionisation energy is correct?
  - (a) Be > B > C > N > O
- (b) B < Be < C < O < N
- (c) B < Be < C < N < O
- (d) B < Be < N < C < O
- 7. Which of the elements Na, Mg, Si and P would have the greatest difference between the first and second ionisation enthalpies?
  - (a) Na

(b) Mg

(c) Si

- (d) P
- 8. The first ionisation energy of Mg, Al, P and S follows the
  - (a) Mg < Al < P < S
- (b) Al < Mg < P < S
- (c) Al < Mg < S < P
- (d) Mg < Al < S < P

## THOUGHT 3

The amount of energy released when an electron is added to an isolated gaseous atom to produce a monovalent anion is called electron affinity or first electron affinity or electron gain enthalpy. The first electron affinity is given a negative sign as the addition of an electron to a neutral atom is an exoergic process. The addition of electron to A requires energy to overcome the force of repulsion. Thus, the second electron affinity is an endoergic process. The magnitude of electron affinity depends on a number of factors such as (i) atomic size (ii) effective nuclear charge (iii) screening effects (iv) half and fully filled orbitals and (v) shape of orbital.

In general, electron affinity increases as the atomic radii decrease in a period. However, there are exceptions when the atoms have stable configurations. In a group, electron affinity decreases as the size increases. However, the members of 3rd period have somewhat higher values than the members in the 2nd period of the same subgroups.

1. What is the  $\Delta H$  of the following reaction?

$$Mg(g) + 2F(g) \longrightarrow Mg^{2+}(g) + 2F^{-}(g)$$
 or  $MgF_2(g)$   
If electron affinity of  $F(g) = -328 \text{ kJ mol}^{-1}$  and  
First ionisation energy of  $Mg = 737.7 \text{ kJ mol}^{-1}$  and  
Second ionisation energy of  $Mg = 1451 \text{ kJ mol}^{-1}$ .

- (a)  $1532.7 \text{ kJ mol}^{-1}$
- (b) 1860.7 kJ mol<sup>-1</sup>
- (c) 2516.7 kJ mol<sup>-1</sup>
- (d) 2844.7 kJ mol<sup>-1</sup>

[Hint: Mg(g) 
$$\longrightarrow$$
 Mg<sup>2+</sup>(g) + 2e  $IE_1 + IE_2 = 2188.7 \text{ kJ mol}^{-1}$   
 $2F(g) + 2e \longrightarrow 2F^ E_A = -2 \times 328 = -656 \text{ kJ mol}^{-1}$   
 $\Delta H = 1532.7 \text{ kJ mol}^{-1}$ 

- 2. Which one of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of the given atomic species? [C.B.S.E. (P.M.T.) 2005]
  - (a) F < Cl < O < S
- (b) S < O < Cl < F
- (c) O < S < F < CI
- (d) Cl < F < S < O
- 3. Which of the following has least electron affinity?
  - (a) Oxygen
- (b) Argon
- (c) Nitrogen
- (d) Boron
- 4. The electron affinities of halogens are:

$$F = -332$$
,  $Cl = -349$ ,  $Br = -324$ ,  $I = -295$  kJ  $mol^{-1}$ 

The higher value of Cl as compared to that of F is due to:

- (a) higher atomic radius of F
- (b) smaller electronegativity of F
- (c) weaker electron repulsion in Cl
- (d) more vacant p-subshell in Cl
- 5. Which of the following species has the highest electron affinity?
  - (a) F

(b) O

(c) Na<sup>+</sup>

- (d) O
- 6. Which of the following processes is endoergic in nature?
  - (a)  $O^- + e \longrightarrow O^{2-}$  (b)  $Cl + e \longrightarrow Cl^-$ (c)  $S + e \longrightarrow S^-$  (d)  $F + e \longrightarrow F^-$
  - (c)  $S + e \longrightarrow S^-$
- (d)  $F + e \longrightarrow F^-$

### THOUGHT 4

The first  $(\Delta_i H_1)$  and the second  $(\Delta_i H_2)$  ionisation enthalpies in kJ mol<sup>-1</sup> and the electron gain enthalpy in kJ mol<sup>-1</sup> of a few elements are given below:

Elements	$\Delta_i H_1$	$\Delta_i H_2$	$\Delta_{\rm eg} H$
(A)	520	7300	-60
(B)	419	3051	-48
(C)	1681	3374	-328
(D)	1008	1946	295

(E) 2372 5251 +48 (F) 738 1451 -40

Answer the following questions. Only one alternative is correct.

- 1. Which one of the above elements is least reactive?
  - (a) (C)

(b) (D

(c) (E)

- (d) (F)
- 2. Which one of the above elements is most reactive metal?
  - (a) (A)

(b) (B)

(c) (F)

- (d) (D)
- 3. Which one of the above elements is most reactive non-metal?
  - (a) (C)

(b) (D)

(c) (E)

- (d) (F)
- 4. The metal which can form a stable binary halide of the formula  $MX_2$  (X = halogen):
  - (a) (A)

(b) (B)

(c) (F)

- (d) (D)
- 5. Which one of above elements is least reactive non-metal?
  - (a) (C)

(b) (D)

(c) (E)

- (d) (F)
- 6. The metal which can form predominantly stable covalent halide of the formula MX (X = halogen):
  - (a) (F)

(b) (B)

(c) (D)

- (d) (A)
- [Hint: (1) The element (E) having very high ionisation enthalpy and positive electron gain enthalpy would be a noble gas, i.e., least reactive.
  - (2) The element (B) would be most reactive metal as it has low ionisation enthalpy and low negative electron gain enthalpy. Probably it is an alkali metal.
  - (3) The element (C) would be most reactive non-metal as it has high negative value of electron gain enthalpy. Probably it is a halogen.
  - (4) The element (F) would form stable  $MX_2$  as it has first two ionisation enthalpies low and low value of electron gain enthalpy, *i.e.*, it belongs to second group.

- (5) The element (D) would be least reactive non-metal.
- (6) The element (A) has low first ionisation enthalpy but very high second ionisation enthalpy. It would be least reactive alkali metal, *i.e.*, lithium which forms covalent MX.]

### **THOUGHT 5**

Atoms of metals have only a few electrons in their valence shells while atoms of non-metals generally have more electrons in their valence shells. Metallic character is closely related to atomic radius and ionisation enthalpy. Metallic character increases from top to bottom in a group and decreases from left to right in a period. Metallic character is inversely related to electronegativity.

**1.** Which of the following groups contains metals, non-metals and metalloids?

(a) Group 1

(b) Group 17

(c) Group 14

- (d) Group 2
- 2. Non-metals belong to:

(a) s-block elements

(b) p-block elements

(c) d-block elements

- (d) f-block elements
- 3. Considering the elements B, C, N, F and Si, the correct order of their non-metallic character is:

(a) B > C > Si > N > F

- (b) Si > C > B > N > F
- (c) F > N > C > B > Si
- (d)  $F > N > C > S_i > B$
- 4. The electronegativities of the following elements increase in the order:
  - (a) C, N, Si, P

(b) N, Si, C, P

(c) Si, P, C, N

- (d) P. Si. N. C
- 5. Considering the elements B, Al, Mg and K, the correct order of their metallic character is :
  - (a) B > Al > Mg > K
- (b) Al > K > B > Mg
- (c) Mg > Al > K > B
- (d) K > Mg > Al > B
- 6. The element with maximum electronegativity belongs to:
  - (a) period 2, group 17
- (b) period 1, group 18
- (c) period 3, group 17
- (d) period 2, group 16

Ause	vers										
Thought 1	1. (d)	2. (d)	3. (a)	<b>4.</b> (b)	5. (c)	6. (d)	7. (c)	8. (b)	9. (a)	10. (c)	
Thought 2	1. (b)	2. (d)	3. (c)	<b>4.</b> (a)	5. (d)	6. (b)	7. (a)	8. (c)	÷ ,		. '
Thought 3	1. (a)	2. (c)	3. (b)	4. (c)	5. (d)	6. (a)					
Thought 4	1. (c)	<b>2.</b> (b)	3. (a)	4. (c)	5. (b)	6. (d)					
Thought 5	1. (c)	2. (b)	3. (d)	4. (c)	5. (d)	6. (a).					

## INTEGER ANSWER Type Questions

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- Among the following, the number of elements showing only one non-zero oxidation state is:
   O, Cl, F, N, P, Sn, Tl, Na, Ti
   [I.I.T. 2010]
- **2.** How many groups are occupied by *p*-block elements in long form of periodic table?
- 3. How many diagonal relationships are present in Mendeleev's periodic table?
- **4.** If for an element (X), the values of successive ionisation energies  $I_1$ ,  $I_2$ ,  $I_3$ ,  $I_4$  and  $I_5$  are 800, 2427, 3658, 25024, 32824 kJ mol<sup>-1</sup> respectively, then the number of valence electrons present are :

- 5. How many unpaired electrons are present in Co3+ ion?
- 6. The first ionisation energy of lithium is 5.41 eV and electron gain enthalpy of chlorine is -3.61 eV. The  $\Delta H$  in kJmol<sup>-1</sup> for the reaction :

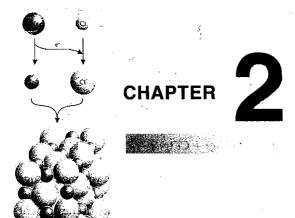
 $Li(g) + Cl(g) \longrightarrow Li^{+}(g) + Cl^{-}(g)$  is  $1.737 \times 10^{x}$  kJ mol<sup>-1</sup> What is the value of x?

- 7. In a period, the element with largest atomic volume belongs to which of the groups?
- 8. The ionistion energy of lithium is 500 kJ mol<sup>-1</sup>. The amount of energy required to convert 70 mg of lithium atoms in gaseous state into Li<sup>+</sup> ions is:

## Answers

- 1. (2) Na exhibits +1 and F exhibits only -1 oxidation state.
- 2. (6) 13, 14, 15, 16, 17 and 18th groups are occupied by *p*-block elements.
- 3. (3) Li Be B Si Mg Al Si (ii) (iii)
- 4. (3) As the difference between  $I_3$  and  $I_4$  is maximum, so the element (X) has three valence electrons as after losing three electrons, it acquires stable inert gas configuration.
- (4) Co<sup>3+</sup>—24 electrons are present. There are four unpaired electrons.

- 6. (2)  $\Delta H = \text{I.P. of Li} + \text{Eg of Cl} = 5.41 3.61 = 1.8 \text{ eV}$   $\Delta H \text{ mol}^{-1} = 1.8 \times 6.023 \times 10^{23} \text{ eV}$   $= 1.8 \times 6.023 \times 10^{23} \times 1.602 \times 10^{-19} \times 10^{-3} \text{ kJ}$   $= 1.737 \times 10^{2} \text{ kJ}$
- (1) In a period, alkali metal which belongs to group I shows largest atomic volume.
- 8. (5)  $70 \text{ mg} = 70 \times 10^{-3} \text{ g} = \frac{70 \times 10^{-3}}{7} = 1 \times 10^{-2} \text{ mole}$ Amount of energy required =  $1 \times 10^{-2} \times 500 \text{ kJ} = 5 \text{ kJ}$



# **Chemical Bonding**

#### Contents:

- 2.1 Introduction
- 2.2 Cause of Chemical Combination
- 2.3 Lewis Symbols of Elements
- **2.4** Electronic Theory of Valency
- 2.5 Electrovalent or Ionic Bond
- 2.6 Determination of Lattice Energy
- 2.7 Types of Ions
- 2.8 Method of Writing Formula of an Ionic Compound
- 2.9 Difference between Atoms and Ions
- 2.10 General Characteristics of Electrovalent Compounds
- 2.11 Variable Electrovalency
- 2.12 Covalent Bond
- 2.13 Covalency
- 2.14 Covalent Compounds
- 2.15 Covalent Molecules of Elements
- 2.16 Characteristics of Covalent Compounds
- 2.17 Comparison between Ionic and Covalent Bonds
- 2.18 Comparison between Ionic and Covalent Compounds
- 2.19 Coordinate Bond
- 2,20 Failure of Octet Rule
- 2.21 Lewis Formulae for Molecules and Polyatomic Ions
- 2.22 Formal Charge
- 2.23 Polarity of Covalent Bond
- 2.24 Dipole Moment
- 2.25 Polarisation (Change of Ionic Character to Covalent Character)
- 2.26 Hydrogen Bonding
- 2.27 Modern Concept of Covalent Bond
- 2.28 Hybridization
- 2.29 Resonance
- 2.30 Prediction of Geometry (Shape) of Covalent Molecules
- 2.31 Valence Shell Electron Pair Repulsion (VSEPR) Theory
- 2.32 Bond Characteristics
- 2.33 Odd Electron Bonds
- 2.34 Molecular Orbital Theory
- 2.35 Metallic Bonding



# 2 INTRODUCTION

From the small number of elements there are derived millions of known compounds, and there are an infinite number possible. This is because there are so many possible ways in which atoms combine to form molecules. This process seems similar to form words of a language from a small number of letters of alphabet. In the formation of words, there are rules of the language which govern the types of possible combination. In the case of atoms, the rules are based on the number and types of electrons which the atoms possess.

Most of the substances are found in nature in the form of clusters or aggregates of atoms. Any such aggregation, in which atoms are held together and which is electrically neutral is called a molecule. The molecules are made of two or more atoms joined together by some force acting between them. The force is termed as a chemical bond. Thus, a chemical bond is defined as a force that acts between two or more atoms to hold them together as a stable molecule or as a force that holds group of two or more atoms together and makes them function as a unit. For example, in water the fundamental unit is the H—O—H molecule, which is described as being held together by the two O—H bonds.



Linus Pauling (1901-1994) won the Nobel Prize in Chemistry in 1954 for his work in chemical bonding

The beginning of our modern theory of bonding can be treated to the concept of valency introduced in 1850. The term valency has been derived from the Latin word 'valentia' which means capacity. Each element was said to have a valency equal to its combining capacity. The number of hydrogen or chlorine atoms with which another atom combines is called its combining capacity. The valency of these two elements was set as, one. Therefore, oxygen which reacts with hydrogen to form H<sub>2</sub>O, was said to have a valency of two. Mg combines with chlorine to form MgCl2, Mg was said to have a valency of two. By using this definition, it is found that elements may have multiple valencies and fractional valencies in certain compounds. For example, nitrogen forms a number of compounds with hydrogen such as NH<sub>3</sub>, N<sub>2</sub>H<sub>4</sub>, N<sub>3</sub>H in which valencies of nitrogen come to 3, 2 and 1/3 respectively.

Thus, the concept of valency as a mere number was very confusing. Later on, the definition of valency was changed. Valency was termed as the number of chemical bonds formed by an atom in a molecule.

The modern concept of valency deals with the interactions between atoms in light of the structure of atoms, *i.e.*, electronic configurations of atoms. The modern concept believes that **electrons are responsible for chemical combination.** It provides tools to find out the answers to the following questions:

- (i) Why do atoms combine?
- (ii) How do atoms combine together?
- (iii) How can the properties of compounds be understood in terms of chemical bonds?

# 2.2 CAUSE OF CHEMICAL COMBINATION

The atoms interact with each other on account of the following reasons:

(i) Decrease in energy: It is a fundamental truth that all natural systems tend to lose potential energy and become more stable. Other things being equal, a system that has stored potential energy is less stable than a system that has none. It is an observed fact that a bonded state is more stable than unbonded state. This is due to the fact that the bonded state has lower potential energy than unbonded state. Hence, when two atoms approach each other, they combine only under the condition that there is a decrease in potential energy.

When two atoms approach each other, new forces of attraction and repulsion come into play. These forces are:

(a) Electrons and nuclei attract one another. Attractive forces are energetically favourable, so an electron attracted to a nucleus is of lower energy and therefore more stable than a free electron.

- (b) Electrons repel each other, raising the energy and reducing the stability.
  - (c) Nuclei repel each other, so reducing the stability also.

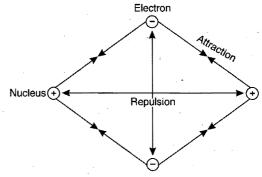


Fig. 2.1 Electrostatic forces in hydrogen molecule

If the net result is attraction, the total potential energy of the system decreases and a chemical bond results. No chemical bonding is possible if net result is repulsion.

(ii) Lewis octet rule: The noble gases are known for their lack of chemical activity. There are no known compounds of helium, neon and argon. Why are these elements so unreactive towards other elements? All these elements have electronic structures that consist of filled cutermost shells. Except for helium, whose electronic configuration is  $1s^2$ , the s-and p-subshells of the highest energy level contain a total of eight electrons. It is, therefore, concluded that  $s^2p^6$  configuration in the outer energy level constitutes a structure of maximum stability and therefore, of minimum energy.

The atoms of all elements when enter into chemical combination try to attain noble gas configuration, *i.e.*, they try to attain either 2 electrons (when only one energy shell) or 8 electrons in their outermost energy level which is of **maximum stability** and hence of **minimum energy**. The tendency of atoms to achieve eight electrons in their outermost shell is known as **Lewis octet rule**. Octet rule was the basis of electronic theory of valency.

Noble gas	Atomic number	Electronic configuration	Configuration of outer energy level
He	2	$1s^2$	$1s^2$
Ne	10	$1s^2$ , $2s^2$ $2p^6$	$2s^2 2p^6$
Ar	18	$1s^2$ , $2s^2 2p^6$ , $3s^2 3p^6$	$3s^2 3p^6$
Kr	36	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$	$4s^2 4p^6$
Xe	54	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ , $5s^2$ $5p^6$	$5s^2 5p^6$
·· Rn	86	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ , $5s^2$ $5p^6$ $5d^{10}$ , $6s^2$ $6p^6$	$6s^2 6p^6$

## 2.3 LEWIS SYMBOLS OF ELEMENTS

Chemical bonding mainly depends on the number of electrons present in the outermost energy level. These electrons are termed as valency electrons. The electronic configuration of sodium (Na) is 2, 8, 1 and that of sulphur has (S) 2, 8, 6. Thus, sodium has one valency electron while sulphur has six valency electrons. In the case of representative elements, the group number (Modern Mendeleev's periodic table) is equal to the number of valency electrons.

The valency electrons in atoms are shown in terms of Lewis symbols. To write Lewis symbol for an element, we write down its symbol surrounded by a number of dots or crosses equal to the number of valency electrons. Paired and unpaired valency electrons are also indicated. The Lewis symbols for hydrogen, sodium, nitrogen, oxygen and chlorine may be written as:

Generalised, Lewis symbols for the representative elements are given in the following table:

#### 2.4 ELECTRONIC THEORY OF VALENCY

The electronic theory of valency owes its rise to the recognition of the existence of electrons in an atom. It was suggested that electrons themselves are responsible for chemical combination. Kossel and Lewis formulated a comprehensive statement which was completed by Langmuir and called electronic theory of valency. The main points of the theory are:

- (i) Valency of an atom depends mainly on the number of electrons present in the outermost orbit. These electrons are termed as valency electrons.
- (ii) Electronic configuration of noble gases is stable, *i.e.*, eight electrons are present in the outermost orbit (except helium having 2 electrons). These gases are chemically inert and do not form any compound.

- (iii) Atoms having less than 8 electrons in the outermost orbit are chemically active. It is the tendency of these atoms to achieve 8 electrons in the outermost orbit. [Hydrogen, lithium, beryllium try to achieve helium configuration.] The number of electrons which take part determines the valency of the atom.
- (iv) There are two ways by which the atoms can acquire noble gas configuration or 8 electrons in the outermost energy level.
  - (a) By losing or accepting electrons.
  - (b) By sharing electrons.

Sharing may be of two types:

- 1. Equal contribution of electrons is made by two atoms and these electrons are then shared equally to form covalent bond, or
- 2. Contribution of an electron pair is made by one atom and both the electrons are shared equally by the two atoms to form coordinate bond. The theory may be summarised in the following way. "The union of two or more atoms involving redistribution of electrons in their outer shells (either by transference or sharing) in such a way so that all the atoms acquire the stable noble gas configuration of minimum energy is known as electronic theory of valency."

Corresponding to the above three ways, there are three types of bonds or linkages which hold the atoms together in a molecule.

- (i) Electrovalent or Ionic bond
- (ii) Covalent bond
- (iii) Coordinate bond

# 2.5 ELECTROVALENT OR IONIC BOND

The chemical bond formed between two or more atoms as a result of the transfer of one or more electrons from electropositive to electronegative atom is called **electrovalent bond**. This bond is also called **ionic** or **polar bond**.

The electron transfer results in the formation of cations and anions. The cations are positively charged ions whereas anions are negatively charged ions. Oppositely charged ions are attracted to each other and a bond between them is formed. The bond existing between the oppositely charged ions is called an ionic or electrovalent or polar bond or the bond formed by the electrostatic attraction between positive and negative ions is called an ionic bond. Compounds containing ionic bonds are called ionic, electrovalent or polar compounds.

[Note: Electrovalent bond is not possible between similar atoms. This type of bonding requires two atoms of different nature, one atom should have the tendency to lose electron or electrons, *i.e.*, electropositive in nature and the other atom should have the tendency to accept electron or electrons, *i.e.*, electronegative in nature. Actually ionic bond is not a true bond but just electrostatic attraction between closely packed ions. It is non-directional in nature.]

# Examples of Electrovalent Bond

(i) Potassium chloride: The free potassium atom has one valency electron (electronic configuration 2, 8, 8, 1), *i.e.*,  $4s^1$  whereas, the chlorine atom has seven valency electrons (electronic configuration 2, 8, 7), *i.e.*,  $3s^2$   $3p^5$ . In forming an ionic bond, the potassium atom loses its valency electron which is accepted by chlorine atom. As a result potassium achieves noble gas configuration of argon (2, 8, 8) and becomes a positive ion (K<sup>+</sup>). Chlorine achieves noble gas configuration of argon (2, 8, 8) and acquires a negative charge (Cl<sup>-</sup>). The attraction between potassium ion and chloride ion is an ionic bond.

A shorthand way of showing the formation of potassium chloride from potassium and chlorine atoms involves electron dot symbols.

$$K^{\times}$$
  $Cl: = K^{+}$   $[\times Cl:]$  or  $K^{+}Cl^{-}$  (2, 8, 8, 1) (2, 8, 7) (2, 8, 8) (2, 8, 8)

(ii) Sodium sulphide: Sodium combines with sulphur to form sodium sulphide, Na<sub>2</sub>S. Two sodium atoms, each loses its valency electron, are converted into sodium ions with neon like configuration (2, 8). Sulphur (2, 8, 6) which has six electrons in the valency shell gains two electrons to achieve the argon like configuration (2, 8, 8).

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(iii) Magnesium fluoride: Magnesium combines with fluorine to form  $MgF_2$ . Magnesium atom loses two electrons and is converted into magnesium ion  $(Mg^{++})$  with neon like configuration (2, 8).

Each fluorine atom having seven electrons in valency shell requires one electron to acquire neon configuration (2, 8).

In all ionic compounds, the electrons lost by one or more atoms in achieving the noble gas configuration of a cation are accepted by the requisite number of companion atoms to achieve noble gas configuration of the anions. Thus,

(number of cations formed)  $\times$  (number of electrons lost in forming one cation) = (number of anions formed)  $\times$  (number of electrons gained in forming one anion).

# Conditions for Forming Electrovalent or Ionic Bond

The following conditions favour the formation of an electrovalent bond.

- (i) Number of valency electrons: One atom should possess 1, 2 or 3 valency electrons while the other atom should have 5, 6 or 7 valency electrons. The atom which changes into cation should possess 1, 2 or 3 valency electrons, *i.e.*, it should belong to group IA, IIA or IIIA. It should be metallic or electropositive in nature. The other atom which changes into anion should possess 5, 6 or 7 electrons in the valency shell, *i.e.*, it should belong to group VA, VIA or VIIA. It should be non-metallic or electronegative in nature. The atoms of transition metals can also lose electron or electrons and converted into cations. Thus, they can also form electrovalent bonds but do not acquire inert gas configuration always.
- (ii) Difference in electronegativity: The formation of an electrovalent bond will be easier if the difference in the electronegativities of the two atoms is high. A difference of about 2 is necessary for the formation of an electrovalent bond. The electronegativity of sodium is 0.9 and that of fluorine is 4.0. Since the difference is 3.1 both will readily form an electrovalent bond.
- (iii) Overall decrease in energy: In the formation of an electrovalent bond, there must be overall decrease in energy, *i.e.*, energy must be released. Energy changes are involved in the following steps:
- (a) Energy equivalent to ionisation energy is required to convert a neutral isolated gaseous atom into a cation.

$$A + \text{ionisation energy} = A^+ + e^- \qquad \dots \text{(i)}$$

Lower the value of ionisation energy of an atom, greater will be the ease of formation of the cation from it, *i.e.*, one atom should have low value of ionisation energy.

(b) Energy equivalent to **electron affinity** is released when an electron is added to a neutral isolated gaseous atom to make it univalent anion.

$$B + e^{-} = B^{-} +$$
electron affinity ...(ii)

Higher the value of electron affinity of the atom, greater the ease of formation of the anion from it, *i.e.*, other atom should have high value of electron affinity.

(c) Lattice energy: Cation and anion attract each other by electrostatic force of attraction to give a molecule  $A^+B^-$ .

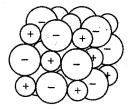


Fig. 2.2 Crystals of ionic compounds

Since the electrostatic field of a charged particle extends in all directions, a positive ion is surrounded by a number of negatively charged ions while each negative ion similarly surrounded by a number of positive ions. These cations and anions arrange systematically in an alternating cation-anion pattern as shown in Fig. 2.2. This is called a crystal lattice. This process of clustering ions increases the force of attraction and thus potential energy decreases. The energy released when the requisite number of positive and negative ions are condensed into crystal to form one mole of the compound is called lattice energy (III step). Higher the lattice energy, greater will be the ease of forming an ionic compound. If the energy released in steps (II) and (III) is greater than the energy used in step (I), the formation of an ionic compound will be favoured.

The value of lattice energy depends on the charges present on the two ions and the distance between them. According to Coulomb's law, the force of attraction (F) between two oppositely charged ions in air with charges equal to  $q_1$  and  $q_2$  and separated by a distance d is given by,

$$F = \frac{1}{4\pi\varepsilon_0 K} \frac{q_1 q_2}{d^2}$$

where d is equal to sum of ionic radii of the two ions and K is dielectric constant of medium.

$$F = \frac{1}{4\pi\varepsilon_0 K} \frac{q_1 q_2}{(r_A^+ + r_B^-)^2}$$

The value of F increases if (i)  $q_1$  and  $q_2$  are high and (ii)  $(r_A^+ + r_B^-)$  is small.

The stability of the ionic compound and the strength of the ionic bond depends on the value of F. Higher the value of F, greater shall be the stability of the ionic compound and hence greater shall be the strength of the ionic bond. For example, NaCl is more stable than CsCl as  $(r_{Na}^+ + r_{Cl}^-)$  is less than  $(r_{Cs}^+ + r_{Cl}^-)$ . MgO is more stable than NaCl as the product  $q_1q_2$  is four times more in MgO than NaCl.

The lattice energy can also be defined as the energy required to separate one mole crystal of an ionic compound into gaseous ions.

$$MX_{(s)} \xrightarrow{+L.E.} M_{(g)}^+ + X_{(g)}^-$$

Theoretically, lattice energy is given by Born-Lande equation.

$$L.E. = \frac{NoMZ^+Z^-e^2}{r} \left[ 1 - \frac{1}{n} \right]$$

where No = Avogadro's number

M = Madelung constant (depends on crystal structure)

 $Z^{+}$  and  $Z^{-}$  = Charges on cation and anion

e = charge on the electron,

 $r = r^+$  (radius of cation) +  $r^-$  (radius of anion)

n = Born constant (depends on the electronic configuration of ions)

Note: In a number of cases, the results obtained from Born-Lande equation are different than experimental values.

Thus, the Born-Lande equation is not perfect and needs modification.

#### Conclusions

- (i) An ionic bond is purely electrostatic in nature.
- (ii) Its formation is favoured by:
- (a) **Low ionisation potential (I.P.)** of the element that forms a cation on losing electron(s). The element should be metal, *i.e.*, electropositive in nature.
- (b) **High electron affinity (E.A.)** of the element that forms an anion on gaining electron(s). The element should be non-metal, *i.e.*, electronegative in nature.

- (c) **High lattice energy (L.E.):** The energy released when isolated ions form a crystal. The value of lattice energy depends on the charges present on the two ions and distance between them. It shall be high if charges are high and ionic radii are small.
- (d) The summation of three energies should be negative, *i.e.*, energy is released.

I.P. + E.A. + L.E. = 
$$-ive$$

- (iii) Highly electropositive elements of groups I and II combine with highly electronegative elements of VI and VII (or 16th and 17th) groups to form electrovalent or ionic compounds. Halides, oxides, sulphides, nitrides and hydrides of alkali and alkaline earth metals are generally ionic.
- (iv) Greater the difference of electronegativity between two atoms, higher will be the possibility of ionic bond formation.
- (v) **Electrovalency**: The capacity of an element to form electrovalent or ionic bond is termed as **electrovalency**. The capacity is measured in terms of the electrons lost or accepted. Thus, electrovalency of an element is equal to the number of electrons lost by an atom of the element or gained by the atom of the element as to acquire inert gas configuration. The elements which lose electron or electrons show positive electrovalency and the elements which gain electron or electrons show negative electrovalency. Generally positive and negative signs are not used in practice and only the number is taken to represent electrovalency.

Element	No: of ele- ctrons lost or gained by an atom	Electro- valency	Change in electronic configuration
Na	1 (lost)	1 (Monovalent)	2, 8, 1 to 2, 8 (Na <sup>+</sup> )
K	1 (lost)	1 (Monovalent)	2, 8, 8, 1 to 2, 8, 8 (K <sup>+</sup> )
Mg	2 (lost)	2 (Divalent)	2, 8, 2 to 2, 8 (Mg <sup>++</sup> )
Ca	2 (lost)	2 (Divalent)	2, 8, 8, 2 to 2, 8, 8 (Ca <sup>++</sup> )
Al	3 (lost)	3 (Trivalent)	2, 8, 3 to 2, 8 (A1 <sup>+++</sup> )
F	1 (gained)	1 (Monovalent)	2, 7 to 2, 8 (F <sup>-</sup> )
Cl	1 (gained)	1 (Monovalent)	2, 8, 7 to 2, 8, 8 (C1 <sup>-</sup> )
О	2 (gained)	2 (Divalent)	2, 6 to 2, 8 (O <sup></sup> )
S	2 (gained)	2 (Divalent)	2, 8, 6 to 2, 8, 8 (S <sup></sup> )
N	3 (gained)	3 (Trivalent)	2, 5 to 2, 8 (N)

# 2.6 DETERMINATION OF LATTICE ENERGY

The lattice energy of an ionic solid is determined experimentally by a process known as **Born-Haber cycle**. This cycle is based on Hess's law, *i.e.*, the formation of an ionic crystal may occur either by direct combination of the elements or by an alternate process in which the following steps are involved. In both cases energy involved is the same.

- (i) The reactants are converted into gaseous state.
- (ii) The gaseous atoms are converted into ions.
- (iii) The gaseous ions are combined to form ionic compound.

For example, the formation of *KF* can occur either directly or in steps.

## **Direct Combination**

$$K(s) + \frac{1}{2}F_2(g) \longrightarrow KF(s)$$

 $\Delta H$  or heat of formation = -562.6 kJ mol<sup>-1</sup>

## In Steps:

(i) Conversion of solid potassium into gaseous state.

$$K(s) \longrightarrow K(g)$$

H.A. or heat of atomisation =  $+89.6 \text{ kJ mol}^{-1}$ 

(ii) Formation of a cation.

$$K(g) \longrightarrow K^+(g) + e^-$$

I.P. or first ionisation potential =  $+419.0 \text{ kJ mol}^{-1}$ 

(iii) Conversion of molecular fluorine into gaseous atomic fluorine.

$$\frac{1}{2}F_2(g) \longrightarrow F(g)$$

1/2 H.D. or 1/2 (heat of dissociation) = + 1/2 (158.2) = 79.1 kJ mol<sup>-1</sup>

(iv) Formation of anion.

$$F(g) + e^{-} \longrightarrow F^{-}(g)$$

E.A. or first electron affinity =-332.6 kJ mol<sup>-1</sup>

(v) Combination of  $K^+(g)$  and  $F^-(g)$  to form KF(s).

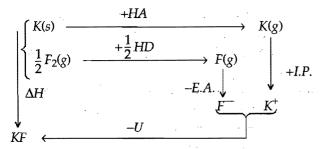
$$K^+(g) + F^-(g) \longrightarrow KF(s)$$

L.E. or lattice energy = -U kJ mol<sup>-1</sup>

On the basis of Hess's law

$$-562.6 = 89.6 + 419.0 + 79.1 - 332.6 - U$$
  
 $U = 817.7 \text{ kJ mol}^{-1}$ ,  
*i.e.*, lattice energy of  $KF = -817.7 \text{ kJ mol}^{-1}$ 

Born-Haber cycle for formation of *KF*(*s*) may be represented as:



Lattice energies of some ionic compounds:

Name of the compound	Lattice energy in kJ mol <sup>-1</sup>	Name of the compound	Lattice energy in kJ mol <sup>-1</sup>
NaCl	769	NaBr	732
KCl	701	CaBr <sub>2</sub>	2132
MgCl <sub>2</sub>	2326	LiI	730
BaCl <sub>2</sub>	2033	NaI	682
Na <sub>2</sub> O	2481	MgI <sub>2</sub>	1944
MgO	37.95	BaI <sub>2</sub>	1831
CaO	3414	CaF <sub>2</sub>	2630
BaO	3029	AlCl <sub>3</sub>	5492

From the above table, it is clear that lattice energy is affected by both the charge and size of the ions. Compounds with higher charges have large lattice energies and lattice energy decreases as the size of one or both the ions, *i.e.*, cation and anion, increases. In general, the compounds having high values of lattice energy possess the following characteristics:

- (i) High stability
- (ii) High melting points
- (iii) Low solubility in water (If lattice energy is higher than hydration energy).

# 2.7 TYPES OF IONS

The following types of ions are encountered.

- (i) Ions with inert gas configuration: The atoms of the representative elements of group I, II and III by complete loss of their valency electrons and the elements of group V, VI and VII by gaining 3, 2 and 1 electrons respectively form ions either with  $ns^2$  configuration or  $ns^2p^6$  configuration.
- (a) Ions with  $1s^2$  (He) configuration:  $H^-$ ,  $Li^+$ ,  $Be^{2+}$ , etc. The formation of  $Li^+$  and  $Be^{2+}$  is difficult due to their small size and high ionisation energy.
- (b) Ions with  $ns^2p^6$  configuration: More than three electrons are hardly lost or gained in the ion formation.

Cations :  $Na^+$ ,  $Ca^{2+}$ ,  $Al^{3+}$ , etc. Anions :  $Cl^-$ ,  $O^{2-}$ ,  $N^{3-}$ , etc. (ii) Ions with pseudo inert gas configuration: The  $\rm Zn^{2+}$  ion is formed when zinc atom loses its outer 4s electrons. The outer shell configuration of  $\rm Zn^{2+}$  ion is  $3s^23p^63d^{10}$ . The  $ns^2np^6nd^{10}$  outer shell configuration is often called pseudonoble gas configuration which is considered as stable one.

(iii) Exceptional configuration: Many d- and f- block elements produce ions with configurations different than the above two. Ions like Fe<sup>3+</sup>, Mn<sup>2+</sup>, etc., attain a stable configuration half filled d-orbitals.

Fe<sup>3+</sup> 
$$3s^2 3p^6 3d^5$$
;  $Mn^{2+} 3s^2 3p^6 3d^5$ 

Examples of other configurations are many.

Ti<sup>2+</sup> 
$$(3s^2 3p^6 3d^2)$$
; V<sup>2+</sup>  $(3s^2 3p^6 3d^3)$   
Cr<sup>2+</sup>  $(3s^2 3p^6 3d^4)$ ; Fe<sup>2+</sup>  $(3s^2 3p^6 3d^6)$ 

However, such ions are comparatively less stable.

- (iv) Ions with  $ns^2$  configuration: Heavier members of groups III, IV and V lose p-electrons only to form ions with  $ns^2$  configuration.  $TI^+$ ,  $Sn^{2+}$ ,  $Pb^{2+}$ ,  $Bi^{3+}$  are the examples of this type. These are stable ions.
- (v) Polyatomic ions: The ions which are composed of more than one atom are called polyatomic ions. These ions move as such in chemical reactions. Some common polyatomic ions are:

$$\mathrm{NH}_{4}^{+}(\mathrm{Ammonium});$$
  $\mathrm{NO}_{3}^{-}(\mathrm{Nitrate});$   $\mathrm{PO}_{4}^{3-}(\mathrm{Phosphate});$   $\mathrm{SO}_{4}^{2-}(\mathrm{Sulphate});$   $\mathrm{SO}_{3}^{2-}(\mathrm{Carbonate});$   $\mathrm{SO}_{3}^{2-}(\mathrm{Sulphite}),$  etc.

The atoms within the polyatomic ions are held to each other by covalent bonds.

The electrovalencies of an ion (any type) is equal to the number of charges present on it.

# 2.8 METHOD OF WRITING FORMULA OF AN IONIC COMPOUND

In order to write the formula of an ionic compound which is made up of two ions (simple or polyatomic) having electrovalencies x and y respectively, the following points are followed:

- (i) Write the symbol of the ions side by side in such a way that positive ion is at the left and negative ion at the right as *AB*.
- (ii) Write their electrovalencies in figures on the top of each symbol as  $A^xB^y$ .
- (iii) Divide their valencies by H.C.F.
- (iv) Now apply criss cross rule as  $A \bowtie B$ , *i.e.*, formula  $A_yB_x$ .

#### Examples:

Calcium chloride $ \begin{array}{cccccccccccccccccccccccccccccccccc$	- Total Prob	and the second of the second o
Potassium phosphate $ \begin{array}{ccccccccccccccccccccccccccccccccccc$	Calcium chloride	$\begin{array}{c} 2 \\ Ca \end{array} \begin{array}{c} 1 \\ C1 = CaCl_2; \end{array}$
Magnesium nitride $\begin{array}{cccccccccccccccccccccccccccccccccccc$	Aluminium oxide	$\begin{array}{c} 3 \\ \text{Al} & O = \text{Al}_2\text{O}_3; \end{array}$
Magnesium nitride $ \begin{array}{cccccccccccccccccccccccccccccccccc$	Potassium phosphate	$ \begin{array}{c} 1 \\ K \end{array} $ $ \begin{array}{c} 3 \\ PO_4 = K_3 PO_4; \end{array} $
Calcium oxide CaO or $Ca \sim 1$ $Ca \sim 0 = CaO;$ $Ca \sim 2$	Magnesium nitride	0 0
Ammonium sulphate $1 \times 2$ $NH_4 \times SO_4 = (NH_4)_2SO_4$	2 2 Calcium oxide CaO or	$1 \setminus 1$
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Ammonium sulphate	$\frac{1}{NH_4}$ $\frac{2}{SO_4} = (NH_4)_2 SO_4$

The following table summarises general formulae of the binary ionic compounds formed by representative elements:

Metal	Non-metal	General formula	Ions present	Example
IA	VIIA	MX	M <sup>+</sup> X <sup>-</sup>	NaCl
IIA	VIIA	$MX_2$	$M^{2+}2X^{-}$	CaCl <sub>2</sub>
IIIA	VIIA	$MX_3$	$M^{3+}3X^{-}$	AlF <sub>3</sub>
IA	VIA	$M_2X$	$2M^{+}X^{2-}$	$K_2S$
IIA	VIA	MX	$M^{2+}X^{2-}$	CaO
IIIA	VIA	$M_2X_3$	$2M^{3+}3X^{2-}$	$Al_2O_3$
IA	VA ·	$M_3X$	3M <sup>+</sup> X <sup>3</sup>	Na <sub>3</sub> P
IIA	VA	$M_3X_2$	$3M^{2+}2X^{3-}$	$Mg_3N_2$
IIIA	VA	MX	$M^{3+}X^{3-}$	AlP

# 2.9 DIFFERENCE BETWEEN ATOMS AND IONS

The following are the points of difference between atoms and ions:

	Atoms	Ions	
1.	Atoms are perfectly neutral in nature, i.e., number of protons equal to number of electrons.  Na (protons 11, electrons 11)	Ions are charged particles, cations are positively charged, <i>i.e.</i> , number of protons more than the number of electrons. Anions are negatively charged, <i>i.e.</i> , number of protons less than the number of electrons.  Na <sup>+</sup> (protons 11, electrons 10) CI <sup>-</sup> (protons 17, electrons 18)	
2.	Except noble gases, atoms have less than 8 electrons in the outermost orbit,	Ions have generally 8 electrons in the outermost orbit, <i>i.e.</i> , $ns^2np^6$ configuration.	
	Na 2, 8, 1; Ca 2, 8, 8, 2 Cl 2, 8, 7; S 2, 8, 6	Na <sup>+</sup> 2, 8; Cl <sup>-</sup> 2, 8, 8 Ca <sup>2+</sup> 2, 8, 8	
3.	Chemical activity is due to loss or gain or sharing of electrons as to acquire noble gas configuration.	The chemical activity is due to the charge on the ion. Oppositely charged ions are held together by electrostatic forces.	

Note: There is a difference in their relative sizes. A positive ion is always smaller and a negative ion is always larger than the corresponding atom.

Na 1.54 Å , *i.e.*, Na<sup>+</sup> < Na 
$$\begin{array}{c} \text{Cl } 0.99 \text{ Å} \\ \text{Cl}^- 1.81 \text{ Å} \end{array}$$
 , *i.e.*, Cl<sup>-</sup> > Cl

# 2.10 GENERAL CHARACTERISTICS OF ELECTROVALENT COMPOUNDS

The compounds having electrovalent bonds are called electrovalent compounds. The following are some of the general properties shown by these compounds:

(i) Crystalline nature: Electrovalent compounds are usually crystalline in nature. The constituent units in an ionic crystal are ions and not molecules. These ions are arranged together in a regular way in an ionic lattice. Force of attraction between the ions is non-directional and extends in all directions. Thus, electrovalent compounds consist of three dimensional solid aggregates. Normally each ion is surrounded by a number of oppositely charged ions and this number is called the coordination number. The coordination numbers of positive and negative ions are the same if there are equal number of both the ions as in NaCl. The geometry of the ionic crystal depends on radius ratio of the cation and anion  $(r_c + /r_{g^-})$ . In the case of NaCl crystal, the coordination number is six that is each Na<sup>+</sup> ion is surrounded by equally spaced six ClT ions placed at the corners of regular octahedron and similarly each Cl ion is surrounded by six equally spaced Na<sup>+</sup> ions placed at the corners of an octahedron (see Fig. 2.3 and 2.4). The shape of NaCl unit cell is cubical.

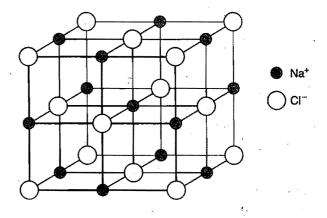


Fig. 2.3 Actual compact structure of sodium chloride crystals

As electrovalent compounds have closed packed structures and ions have no freedom of movement, these are not found in liquid or gaseous states under ordinary conditions of temperature and pressure and exist as solids.

Electrovalent compounds have low volatility and high stability because strong electrostatic forces of attraction bring these ions very close to one another, thereby decreasing the volume of the crystal and hence, these compounds have high density.

(ii) Melting and boiling points: Due to strong electrostatic forces of attraction, the ions are held tightly in their positions in the crystal lattice. To dislodge the ions from their positions, a considerable amount of energy is needed to overcome the forces of attraction. Thus, electrovalent compounds possess high melting and boiling points. Melting point of ionic solid is sharp and fixed. Cooling curve of ionic solids is also not smooth (see cooling curve on Page 76).

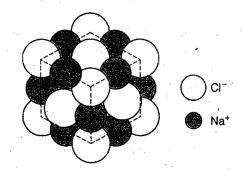


Fig. 2.4 Cubical structure of sodium chloride crystal

(iii) Hard and brittle: Electrovalent compounds are hard in nature. The hardness is due to strong forces of attraction between oppositely charged ions which keep them in their alloted positions. The brittleness of the crystals is due to movement of a layer of a crystal on the other layer by application of external force when like ions come infront of each other. The forces of repulsion come into play. The breaking of crystal occurs on account of these forces or repulsion.

(iv) Solubility: Electrovalent compounds are fairly soluble in polar solvents and insoluble in non-polar solvents. The polar solvents have high values of **dielectric constants.\*** Water, the polar solvent, is one of the best solvents as it has a high value of dielectric constant. Due to high value of dielectric constant, the electrostatic force of attraction between the ions decreases and these ions get separated and ultimately solvated by the molecules of the solvent. The non-polar solvents have very low value of dielectric constants\* and are not capable of dissolving electrovalent compounds.

The values of dielectric constants of some of the compounds are given below:

Compound Water Methyl Alc. Ethyl Alc. Acetone Ether Dielectric constant 81 35 27 21 4.1

Capacity to dissolve electrovalent compounds decreases

The solubility in polar solvents like water can also be explained by saying that the molecule of water is a dipole.

The positive end of the dipole interacts with the negative ion of the electrovalent compound and the negative end of the dipole interacts with the positive ion of the same electrovalent compound as shown in Fig. 2.5. Water molecules pull

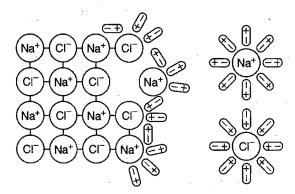


Fig. 2.5 Solvation of NaCl in water

the ions from the crystal lattice. These ions are then surrounded by water dipoles with the oppositely charged ends directed towards them. These solvated ions lead an independent existence and are thus dissolved in water.

The solubility of an electrovalent compound in a polar solvent can also be explained on the basis of lattice and solvation (hydration in case if water is solvent) energies. The electrovalent compound dissolves in a solvent if the value of solvation energy is higher than the lattice energy of the electrovalent compound. When the compound is dissolved in a solvent, first the compound is broken down into ions. The energy required for this process is called lattice energy.

$$AB$$
 + Lattice energy =  $A^+$  +  $B^-$ 

These ions are surrounded by solvent molecules. This process is called solvation. This process is exothermic.

$$A^+ + x(\text{solv.}) \longrightarrow [A (\text{solv.})_x]^+ + \text{energy}$$
  
 $B^- + y(\text{solv.}) \longrightarrow [B (\text{solv.})_y]^- + \text{energy}$ 

The value of solvation energy depends on the relative size of the ions. Smaller the ion more of solvation, hence solvation energy will be high. The non-polar solvents do not form solvated ions and thus no energy is released. Hence, solubility of electrovalent compounds in non-polar solvents is not possible. It is notable point that if an electrovalent compound dissolves in non-polar solvent then colloidal solution is formed, *e.g.*, NaCl form colloidal solution in kerosene.

(v) Electrical conductivity: Electrovalent solids do not conduct electricity. The reason is that the ions, on account of electrostatic forces of attraction, remain intact occupying fixed positions in the crystal lattice. The ions, thus, do not move where electric current is applied.

<sup>\*</sup>The dielectric constant of a solvent is defined as its capacity to weaken the force of attraction between the electrical charges immersed in that solvent.

When electrovalent compounds are melted or dissolved in a polar solvent, the ions become mobile. They are attracted towards the respective electrodes and act as carrier of electric current. Thus, electrovalent compounds in the molten state or in solution conduct electricity.

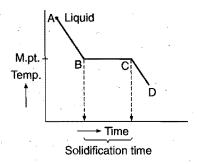
- (vi) Space isomerism: The electrovalent bond is nonrigid and non-directional. Thus, the electrovalent compounds do not show space isomerism or stereo-isomerism.
- (vii) Isomorphism: Compounds having same electronic structures are isomorphous to each other. For example, sodium fluoride and magnesium oxide are isomorphous to each other.

Potassium sulphide, potassium chloride and calcium chloride are isomorphous to each other.

(viii) Ionic reactions: Electrovalent compounds furnish ions in solution. The chemical reactions are due to the presence of these ions. Such reactions are fast. For example, SO<sub>4</sub><sup>2</sup>-ions present in Na<sub>2</sub>SO<sub>4</sub> solution, form white precipitate of BaSO<sub>4</sub> as soon as BaCl<sub>2</sub> solution is added to it.

$$Na_2SO_4 \longrightarrow 2Na^+ + SO_4^2$$
 $BaCl_2 \longrightarrow Ba^{2+} + 2Cl^ Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4 \downarrow$ 
White precipitate

(ix) Cooling curve: Cooling curve of an ionic compound is not smooth, it has two break points corresponding to time of solidification.



# 2.11 VARIABLE ELECTROVALENCY

Certain elements (metals) show more than one electrovalency in their electrovalent compounds. The atoms of these elements lose different number of electrons under different conditions, thereby showing variable electrovalency. The following are two reasons for variable electrovalency:

(i) Instability of the core: The residue configuration left after the loss of valency electrons (electrons present in the outermost energy level) is called a core or kernel. In the case of the atoms of transition elements, ions formed after the loss of valency electrons do not possess a stable core as the configuration of outermost shell is not ns<sup>2</sup>np<sup>6</sup> but ns<sup>2</sup>np<sup>6</sup>d <sup>1 to 10</sup>. The outershell generally loses one or more electrons giving rise to metal ions of higher valencies. The variable valencies of iron and copper can be explained on this basis.

Fe 26 2, 8, 8 + 6, 2 
$$3s^2 3p^6 3d^6$$
,  $4s^2$   
Fe<sup>2+</sup> 24 2, 8, 8 + 6  $3s^2 3p^6 3d^6$  (Not stable)  
Fe<sup>3+</sup> 23 2, 8, 8 + 5  $3s^2 3p^6 3d^5$  (Stable)

Thus, iron shows +2 and +3 valencies. The compounds, in which iron is in trivalent state, i.e., ferric compounds are more stable than the compounds in which iron is in divalent state (ferrous compounds). The atom of copper possesses one electron in the outermost shell. It loses this electron to form Cu<sup>+</sup> (cuprous) ion.

Cu 29 2, 8, 18, 1 
$$3s^2 3p^6 3d^{10}$$
, 4s  
Cu<sup>+</sup> 28 2, 8, 18  $3s^2 3p^6 3d^{10}$ 

Cu<sup>+</sup> 28 2, 8, 18  $3s^2 3p^6 3d^{10}$ The  $s^2p^6d^{10}$  configuration is not as stable as  $s^2p^6$ configuration and the nuclear charge is not sufficiently strong to hold all the electrons intact in their positions. Thus, Cu<sup>+</sup> ion loses one more electron to form Cu<sup>2+</sup> (cupric) ion. The Cu<sup>2+</sup> ion is quite stable as the nuclear charge is sufficient to hold 27 electrons intact.

Cu<sup>2+</sup> 2, 8, 17 
$$3s^2 3p^6 3d^9$$

Thus, cupric compounds are more stable than cuprous compounds.

The above two explanations fail to account why

- (a) Co<sup>2+</sup> ion cannot be easily converted into Co<sup>3+</sup> ion like Fe<sup>2+</sup> ion.
- (b) Zn2+ ion does not lose one more electron as its configuration  $(3s^2 3p^6 3d^{10})$  is similar to Cu<sup>+</sup> ion.

In general, we can say that whenever the core is unstable, it loses one or more electrons to show higher valency and if the core is comparatively stable it always resists the loss of

The cores of Co<sup>2+</sup> ion and Zn<sup>2+</sup> ion are comparatively stable as the nuclear charges are sufficient to hold all the electrons intact in their positions. Co<sup>2+</sup> ion changes into Co<sup>3+</sup> ion in presence of an oxidising agent, but cobaltous compounds are comparatively more stable than cobaltic compounds.

[Note: Cu2+ is more stable in aqueous solution than Cu+ due to high hydration energy.]

(ii) Inert pair effect: Some of heavier representative elements of third, fourth and fifth groups having configurations of the outermost shell  $ns^2np^1$ ,  $ns^2np^2$  and  $ns^2np^3$ show valencies with a difference of 2, i.e., (1; 3), (2; 4), (3; 5), respectively. In the case of lower valencies, only the electrons present on p-subshell are lost and  $ns^2$  electrons remain intact. The reluctance of s-electron pair to take part in bond formation is known as the **inert pair effect**. A partial explanation of the inert pair effect is due to the fact that outer  $ns^2$  electrons penetrate to some extent to penultimate orbit consisting 18 electrons thereby attracted strongly towards nucleus. Inert pair effect increases in a group as the atomic number increases.

(III group) 2, 8, 18, 32, 18,  $6s^2 6p^1$ Tl  $T1^+$ 2, 8, 18, 32, 18, 6s<sup>2</sup> Only 6p electron is lost (IV group) 2, 8, 18, 18,  $5s^2 5p^2$ Sn Sn<sup>2+</sup>  $2, 8, 18, 18, 5s^2$ Only 5p electrons are lost (IV group) 2, 8, 18, 32, 18,  $6s^2$   $6p^2$ Pb 2, 8, 18, 32, 18,  $6s^2$  Only 6p electrons are lost (V group) 2, 8, 18, 32, 18,  $6s^2 6p^3$ Bi Bi<sup>3+</sup> 2, 8, 18, 32, 18,  $6s^2$  Only 6p electrons are lost

When sufficient energy is available, the s-electrons also enter into bond formation and higher valencies are observed. This tendency to show higher valencies is less in the case of Tl, Pb and Bi but more in the case of comparatively lighter elements such as In, Sn, Sb, etc.

#### **Conclusions**

- 1. In group 13, Ga, In and Tl show variable valencies of +3 and +1. The stability of +3 state decreases while that of +1 state increases. Tl<sup>+</sup> is thus more stable than Tl<sup>3+</sup>.
- 2. In group 14, Ge, Sn and Pb show variable valencies of +4 and +2. The stability of +4 state decreases while that of +2 state increases. Thus, Ge<sup>4</sup> is more stable than Ge<sup>2+</sup> while Pb<sup>2+</sup> is more stable than Pb<sup>4+</sup>.
- 3. In group 15, P, As, Sb and Bi show variable valencies of +5 and +3. The stability of +5 state decreases while that of +3 state increases.

# 2.12 COVALENT BOND

The second mode of combination was first proposed by Lewis, in 1916, that there are atoms which attain noble gas configuration by sharing one or more electron pairs when each atom contributes equally. The pair or pairs of electrons become a common property of both. Such a bond is possible between similar and dissimilar atoms. In this bond the atoms do not acquire any charge as the electron or electrons are not lost completely. The electrons, which are shared, occupy such a position in between the nuclei of the two atoms where there is maximum force of attraction from the two nuclei. The bond is, therefore, termed as non-polar bond.

"A chemical bond formed by sharing one or **more** electron pairs between atoms when each atom contributes equally is called a covalent bond."

Covalent bond may be single, double or a triple bond. Double and triple covalent bonds are called **multiple covalent bonds**. Single covalent bond is formed by sharing of only one electron pair. This bond is represented by single dash (—). Double and triple covalent bonds are formed

when atoms bonded together share two or three electron pairs, respectively. These bonds are represented by double dash (=) and triple dash (=) respectively. Some examples of covalent bonding are given below:

(i) Formation of hydrogen molecule: In the formation of hydrogen molecule, each hydrogen atom contributes one electron and then the pair is shared between two atoms. Both the atoms acquire stable configuration of helium. Thus, the molecule consists of one single covalent bond.

$$H^{\times} + {}^{\bullet}H \longrightarrow H \xrightarrow{\times} H$$
 or  $H \longrightarrow H$ 

(ii) Formation of chlorine molecule: Chlorine atom has seven electrons in the valency shell. In the formation of chlorine molecule, each chlorine atom contributes one electron and then the pair of electrons is shared between two atoms. Both the atoms acquire stable configuration of argon.

(iii) Formation of HCl molecule: Both hydrogen and chlorine contribute one electron each and then the pair of electrons is equally shared. Hydrogen acquires the configuration of helium and chlorine acquires the configuration of argon.

$$H^{\times}$$
 .C1:  $H$  .C1 or  $H$ —C1 (2) (2,8,8)

(iv) Formation of water molecule: Oxygen atom has 6 valency electrons. It can achieve configuration of neon by sharing two electrons, one with each hydrogen atom.

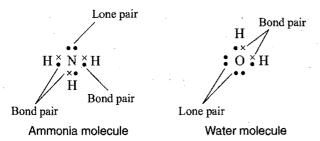
(v) Formation of methane: Carbon has four electrons in the valency shell. It can achieve stable configuration of neon by sharing four electrons with four hydrogen atoms, one with each hydrogen atom. Each hydrogen atom acquires helium configuration.

(vi) Formation of  $O_2$  molecule: Each oxygen atom contributes two electrons and two pairs of electrons are then shared equally. Both the atoms acquire configuration of neon.

(vii) Formation of N<sub>2</sub> molecule: Nitrogen atom has five valency electrons. Both nitrogen atoms achieve configuration of neon by sharing 3 pairs of electrons, *i.e.*, each atom contributes 3 electrons.

$$(2.5) \quad (2.5) \quad (2.8) \quad (2.8) \quad (2.8)$$
 or N\implies N

The shared pairs of electrons present between the atoms are called **bond pairs**. On the other hand, the valency electrons which are not involved in sharing or in the formation of covalent bonds are termed **lone pairs** or **non-bonded electrons**.



#### Conditions for formation of covalent bonds

The following conditions favour the formation of covalent bonds:

- **(i)** Electronegativity: An atom will not transfer the electron or electrons to the other atom if the electronegativity difference between the two atoms is zero or very small (less than 1.6). Such atoms prefer to share electrons, *i.e.*, form covalent bonds.
- (ii) When both the atoms are short in electrons in the valency shell in comparison to stable noble configuration, then such atoms complete the outermost shell by sharing electrons. Except hydrogen which has one electron in valency shell, such atoms have 5, 6 or 7 valency electrons. The non-metals of group VA, VIA and VIIA satisfy this condition.

# 2.13 COVALENCY

It is defined as the number of electrons contributed by an atom of the element for sharing with other atoms as to achieve noble gas configuration. It can also be defined as the number of covalent bonds formed by the atom of the element with other atoms. The usual covalency of an element except hydrogen (which has covalency 1) is equal

to 8-group number of Mendeleev's table to which an element belongs. This is true for the elements belonging to IV, V, VI and VII groups.

Element	Group	(8-Group number)	Covalency
С	IV	8 - 4 = 4	4
Si	ľV	8 - 4 = 4	4
N	V	8 - 5 = 3	3
P	$\mathbf{V}$	8 - 5 = 3	3 ·
Ο .	VI	8 - 6 = 2	2
S	VI	8 - 6 = 2	<b>2</b> ·
$\mathbf{F}$	VII	8 - 7 = 1	1 -
Cl	VII	8 - 7 = 1	1

Generally, the covalency of an element is equal to the total number of unpaired electrons in s- and p-orbitals of the valency shell.

Covalency 15 1 Hydrogen has one unpaired orbital One 2s 2p1 11 11 Fluorine has only one unpaired orbital One 11 11 Oxygen has two unpaired p-orbitals Two Nitrogen has three unpaired p-electrons 1↓ 1 Three

These four elements do not possess *d*-orbitals in their valency shell. However, the elements having vacant *d*-orbitals in their valency shell like P, S, Cl, Br, I, show variable covalency by increasing the number of unpaired electrons under excited conditions, *i.e.*, unpairing the paired orbitals and shifting the electrons to vacant *d*-orbitals. [Such a shifting is not possible in the case of H, N, O and F because *d*-orbitals are not present in their valency shell.]

Phosphorus shows 3 and 5 covalencies.

Phosphorus atom in ground state

Three unpaired electrons covalency = 3

Phosphorus atom in excited state

Five unpaired electrons covalency = 5

Sulphur atom shows 2, 4 and 6 covalencies.

Sulphur atom in ground state

Two unpaired electrons covalency = 2

Sulphur atom in excited state,

(a) When p-orbital is unpaired (first excited state.)

Four unpaired electrons covalency = 4

(b) When s- and p-orbitals are unpaired (second excited state.)  Chlorine shows 1, 3, 5 and 7	Six unpaired electrons covalency = 6 covalencies.	(b) Second excited state when two orbitals are unpaired	Five unpaired electrons covalency = 5
Chlorine atom in ground state	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(c) Third excited state when one s-and two p-orbitals are unpaired	↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑
Chlorine atom in excited state,  (a) First excited state when p-orbital is unpaired	One unpaired electron covalency = 1  Three unpaired electrons covalency = 3	Thus, variable covalency	covalency = 7  is shown by those elements orbitals in their valency shell.

# 2.14 COVALENT COMPOUNDS

The compounds containing a covalent bond or a number of covalent bonds are termed as **covalent compounds**. Compounds such as HCl, CH<sub>4</sub>, CO<sub>2</sub>, SiO<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, PCl<sub>3</sub>, SO<sub>2</sub>, etc., are some of the examples of covalent compounds. All organic compounds and the compounds formed by the combination of two different non-metals are covalent in nature.

# 2.15 COVALENT MOLECULES OF ELEMENTS

Some of elements are known to exist in molecular forms under ordinary conditions. These molecules also possess covalent bond or bonds. For example, halogens, sulphur, oxygen, nitrogen, hydrogen, phosphorus, etc., exist in molecular forms. Carbon and silicon have complex structure. In these structures the atoms are also linked by covalent bonds.

Element	Formula of the molecule	St	ructure
Hydrogen	H <sub>2</sub>	H ∗ H	H—H
Halogens (F, Cl, Br, I)	$X_2$	: X : X :	х—х
Oxygen	O <sub>2</sub>	:0::0:	0=0
Nitrogen	$N_2$	: N : N :	N≔N
Sulphur (Every sulphur atom is linked to two ot S atoms by single covalent bonds.)	S <sub>8</sub> her	s—s s—s	S S S S S S S S S S S S S S S S S S S
Phosphorus (Every phosphorus atom is linked to other three P atoms by single covalent bonds.		P	P
	•	- P	,h,

# 2.16 CHARACTERISTICS OF COVALENT COMPOUNDS

(i) Physical state: Under the normal conditions of temperature and pressure, these exist as gases or liquids of low boiling points. This is due to the fact that very weak forces of attraction (van der Waals' forces) exist between discrete molecules.

Some exist as soft solids if their molecular masses are high. Sulphur, phosphorus, iodine are soft solids.

- (ii) Melting and boiling points: With the exception of few which have giant three dimensional structures such as diamond, carborundum (SiC), silica (SiO<sub>2</sub>), others have relatively low melting and boiling points. This is due to the presence of weak attractive forces between the molecules. On supplying heat energy, the molecules are readily pulled out from these forces and move freely having high kinetic energy.
  - (iii) Crystal structure: These are of three types.
- (a) First type: These are the crystals in which the unit is molecules. The molecules are held by van der Waals' forces. These are readily fusible and volatile. Examples are sulphur, iodine, phosphorus pentoxide, etc.
- (b) Second type: This includes crystals which have separate lattice layers. The best example of this type is graphite. Each atom has three neighbours. It is bonded to two of them by single covalent bonds and to the third by double bond. The bonds tie the atoms very tightly together into a layer. These layers can slide on one another. This accounts for the softness of graphite.
- (c) Third type: This includes crystals in which every atom is bonded to four other atoms by single covalent bonds resulting in the formation of giant structure. Examples are diamond, silicon carbide (SiC), aluminium nitride (AlN). These crystals are very hard and possess high melting points.
- (iv) Electrical conductivity: In general, covalent substances are bad conductors of electricity. Substances which have polar character like HCl in solution, can conduct electricity. Covalent solids having giant molecules, are bad conductors since they do not contain charged particles or free electrons. The graphite can conduct electricity since electrons can pass from one layer to the other.
- (v) Solubility: In general, covalent substances are insoluble in polar solvents like water but soluble in non-polar solvents like benzene, carbon tetrachloride, ether, etc. This is based on the principle, "Like dissolves like". Some of the covalent compounds like alcohols, amines dissolve in water due to hydrogen bonding. Covalent solids having giant molecules are practically insoluble in all solvents.
- (vi) Molecular reactions: Covalent substances show molecular reactions. The reaction rates are usually low because it involves two steps (i) breaking of covalent bonds of the reactants and (ii) establishing of new bonds while the ionic reactions involved only regrouping of ions.
- (vii) Isomerism: The covalent bond is rigid and directional. On account of this, there is a possibility of different arrangements of atoms in space. Covalent compounds can, thus, show isomerism (structural and space).

# 2.17

# COMPARISON BETWEEN IONIC AND COVALENT BONDS

	Ionic bond	Covalent bond
1.	Formed by the transference of electron or electrons from electro positive (metal) to electronegative (non-metal) atoms.  Such a bond is possible between dissimilar atoms.	Formed by sharing of electrons between two non-metal atoms when the electrons are equally contributed by both the atoms. Such a bond is possible between similar and dissimilar atoms.
2.	Consists of electrostatic force between atoms.	Consists of shared pair or pairs of electrons which are attracted by both the nuclei.
3.	Non-rigid and non-directional, does not cause isomerism.	Rigid and directional, causes space and structural isomerism.
4.	It is a weak bond, since the electrostatic force between the ions can be broken easily.	It is strong bond, since the paired electrons cannot be separated easily.
5.	It is polar in nature.	It is non-polar if the electronega-

# 2.18 COMPARISON BETWEEN IONIC AND COVALENT COMPOUNDS

Covalent compounds

Gases, liquids or soft solids under ordinary conditions.	
Low melting and boiling points with the exception of giant molecules.	
Soft and waxy with the exception of giant molecules.	
Usually insoluble in water and in polar solvents. Soluble in non-polar solvents.	
Bad conductors of electricity with few exceptions having layer lat- tice structure.	
Undergo molecular reactions. Rates of reactions are low. Reactions are slow.	

# 2.19 COORDINATE BOND

Ionic compounds

It is a special type of covalent bond in which both the shared electrons are contributed by one atom only. It may be defined as "a covalent bond in which both electrons of the shared pair are contributed by one of the two atoms". Such a bond is also called as dative bond. A coordinate or a dative bond is established between two such atoms, one of which has a complete octet and possesses a pair of valency electrons while the other is short of a pair of electrons.

$$\begin{array}{c} \bullet \bullet \\ A \bullet \bullet \\ \bullet \\ \bullet \end{array} + \begin{array}{c} \bullet \times \times \\ B \times \\ \times \times \end{array} \longrightarrow \begin{array}{c} \bullet \bullet \\ \bullet \\ \bullet \\ \bullet \end{array} \begin{array}{c} \bullet \times \\ \bullet \\ \bullet \\ \times \times \end{array} \end{array}$$
 or  $A \longrightarrow B$ 

This bond is represented by an arrow  $(\rightarrow)$ .

The atom which contributes electron pair is called the **donor** while the atom which accepts it is called **acceptor**.

ote: Coordinate bond after formation is indistinguishable from a covalent bond.

The formation of a coordinate bond can be looked upon as a combination of electrovalent and covalent bonds. The formation may be assumed to have taken place in two steps:

(i) The donor atom loses one electron and transferred to acceptor atom. As a result donor atom acquires a positive charge and the acceptor atom acquires a negative charge.

(ii) These two charged particles now contribute one electron each and this pair is shared by both the atoms.

$$\begin{bmatrix} \vdots & A & \downarrow \\ \vdots & A & \downarrow \end{bmatrix} + \begin{bmatrix} \times \times \\ B & \times \\ \times \times \end{bmatrix} \longrightarrow \begin{bmatrix} \vdots & A^{+} & \vdots & B^{-} \\ B & \times \\ \times \times \end{bmatrix}$$

As the coordinate bond is a combination of one electrovalent bond and one covalent bond, it is also termed as **semi polar bond**.

The compound consisting of the coordinate bond is termed **coordinate compound**. Some examples of coordinate bond formation are given below:

(i) Combination of ammonia and boron trifluoride: Although the nitrogen atom has completed its octet in ammonia, it still has a lone pair of electrons in the valency shell which it can donate. The boron atom in boron trifluoride is short of two electrons which it accepts and completes its octet.

Any atom or ion or molecule which has one unshared electron pair which it can donate is termed as **Lewis base** while those which are capable of accepting the lone pair are termed as **Lewis acids**. In above example ammonia is a Lewis base while boron trifluoride is a Lewis acid.

Note:  $H^+$  ion and cations of transition metals such as  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Cr^{3+}$ ,  $Ni^{2+}$ , etc., act as Lewis acids. The donors are also called as ligands.

(ii) Formation of ammonium ion: Hydrogen ion (H<sup>+</sup>) has no electron and thus accepts a lone pair donated by nitrogen.

(iii) Formation of  $H_2O_2$ : Oxygen in water has two lone pairs of electrons, out of which one is donated to another oxygen atom forming hydrogen peroxide.

(iv) Formation of ozone: Oxygen molecule consists of two oxygen atoms linked by a double covalent bond. Each oxygen atom has two lone pairs of electrons. When one lone pair of electrons is donated to a third oxygen atom which has six electrons, a coordinate bond is formed.

$$0 = 0 + 0 \times \times \times \longrightarrow 0 = 0 \longrightarrow 0$$
Donor Acceptor

(v) Formation of CO: Carbon has four valency electrons and oxygen has six. Two combine to form a double bond and a coordinate bond as to achieve their octet completed.

# **■** Characteristics of Coordinate Compounds

The properties of coordinate compounds are intermediate between the properties of electrovalent compounds and covalent compounds. The main properties are described below:

- (i) Physical state: These exist as gases, liquids and solids under ordinary conditions.
- (ii) Melting and boiling points: Their melting and boiling points are higher than purely covalent compounds and lower than purely ionic compounds.
- (iii) Solubility: These are sparingly soluble in polar solvents like water but readily soluble in non-polar (organic) solvents.
- (iv) Stability: These are as stable as the covalent compounds. The addition compounds are, however, not very stable. It is also a strong bond because the paired electrons cannot be separated easily.

- (v) Conductivity: Like covalent compounds, these are also bad conductors of electricity. The solutions or fused mass do not allow the passage of electricity.
- (vi) Molecular reactions: These undergo molecular reactions. The reactions are slow.
- (vii) Isomerism: The bond is rigid and directional. Thus, coordinate compounds show isomerism.
- (viii) Dielectric constant: The compounds containing coordinate bond possess high values of dielectric constants.

# 2.20 FAILURE OF OCTET RULE

There are several stable molecules known, in which the octet rule is violated, *i.e.*, atoms in these molecules have number of electrons in the valency shell either short of octet or more than octet. Some important examples are:

(i) BeCl<sub>2</sub> molecule: BeCl<sub>2</sub> (beryllium chloride) is a stable molecule. Be atom forms two single covalent bonds with two chlorine atoms, *i.e.*, it attains four electrons in the outer shell.

$$_{\times}$$
 Be  $_{\times}$  +2 •Cl :  $\longrightarrow$  Cl  $_{\times}$  Be  $_{\times}$  Cl  $_{\times}$  Cl -Be-Cl

(ii) BF<sub>3</sub> molecule: Boron atom forms three single covalent bonds with three fluorine atoms, *i.e.*, it attains six electrons in the outer shell.

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(iii) PCl<sub>5</sub> molecule: Phosphorus atom have five electrons in valency shell. It forms five single covalent bonds with five chlorine atoms utilising all the valency electrons and thereby attains 10 electrons in the outer shell.

(iv)  $SF_6$  molecule: Sulphur atom has six electrons in the valency shell. It forms six single covalent bonds with six fluorine atoms utilising all the valency electrons and thereby attains 12 electrons in the outer shell.

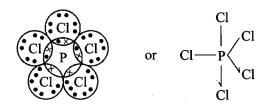
(v)  $IF_7$  molecule: Iodine forms seven single covalent bonds with seven fluorine atoms utilising 7 valency electrons. The iodine atom attains 14 electrons in outermost shell.

To explain the above abnormalities, the following two concepts were introduced:

# 1. Sugden's concept of singlet linkage:

Sugden introduced the idea of singlet linkage in favour of octet rule. According to this concept the maximum number of electrons in the outermost shell of any atom cannot exceed eight. In the molecules of PCl<sub>5</sub>, SF<sub>6</sub>, IF<sub>7</sub>, etc., the central atom is linked with some of the combining atoms by single-electron bonds, called **singlet linkage** while the remaining atoms are linked by the normal two electrons bonds. The bond is represented by a half arrow ( ) with the head pointing from donor towards the acceptor.

In PCl<sub>5</sub>, three chlorine atoms are linked by normal covalent bonds and two chlorine atoms are linked by singlet linkages, thus, phosphorus achieves 8 electrons in the outermost shell.



This structure indicates that the nature of two chlorine atoms is different than the other three as singlet linkage is weaker than normal covalent bond. The above observation is confirmed by the fact that on heating, PCl<sub>5</sub> dissociates into PCl<sub>3</sub> and Cl<sub>2</sub>.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Similarly, in SF<sub>6</sub>, four singlet linkages are present while in IF<sub>7</sub>, six singlet linkages are present.

# 2. Sidgwick's concept of maximum covalency

This rule states that the covalency of an element may exceed four and octet can be exceeded. The maximum covalency of an element actually depends on the period of periodic table to which it belongs. The maximum covalency of the elements is tabulated below:

Period	Elements	Maximum covalency	No. of electrons in the outermost orbit
1st	Н	2	4
2nd	Li to F	4	8
3rd	Na to Cl	. 6	12
4th	K to Br	6	12
$^{5 ext{th}}$ $\}$	Rb onwards and rest of	8	16
6th	the elements	}	,

This rule explains the formation of PCl<sub>5</sub> and SF<sub>6</sub>. This also explains, why nitrogen does not form NF5 or NCl5 because nitrogen belongs to second period and the maximum covalency of nitrogen is four.

# 2.21 LEWIS FORMULAE FOR MOLECULES AND POLYATOMIC IONS

Lewis electron-dot formula of a molecule or a polyatomic ion shows how atoms are bonded with each other. Bonding electrons are indicated either by two dots or by a dash. For instance, a water molecule can be represented by either of the following two diagrams.

Lewis dot formula

Dash formula

Lewis dot formulae show only the number of valency electrons, the number and kinds of bonds, but do not depict the three dimensional shapes of molecules and polyatomic ions. Lewis formulae are based on the fact that the representative elements achieve a noble gas configuration in most of their compounds, i.e., 8 electrons in their outermost shell (except for H<sub>2</sub>, Li<sup>+</sup> and Be<sup>2+</sup> ions which have 2 electrons).

The following steps are followed in constructing dot formulae for molecules and polyatomic ions:

- (i) Write a symmetrical 'skeleton' for the molecules and polyatomic ions.
- (a) The least electronegative element is usually taken as the central element except H.

For example: CO<sub>2</sub> has the skeleton OCO.

(b) Oxygen atoms do not bond to each other except in  $O_2$ , O<sub>3</sub>, the peroxides and superoxides. The phosphate ion

$$(PO_4^{3-})$$
 has the skeleton O  $\stackrel{\circ}{P}$  O.

(c) Hydrogen actually bonds to an oxygen atom and not to the central atom in ternary acids (oxyacids).

For example: Nitrous acid HNO2, has the skeleton HONO. However, there are exceptions to this rule, such as for H<sub>3</sub>PO<sub>2</sub>, the skeleton is H P OH.

H

(d) For polycentred species such as C2H4, the most HH

symmetrical skeleton is used. C C is the skeleton for C<sub>2</sub>H<sub>4</sub>. HH

(ii) Calculate the number of electrons available in the valency shell of all the atoms.

For negatively charged ions add to the total number of electrons equal to the charge on the anion and for positively charged ions, subtract the number of electrons equal to the charge on the cations.

The total number of electrons calculated in this way is represented by symbol A.

For example: A for  $H_2SO_4$ 

 $A = 2 \times 1$  (for hydrogen atoms) + 1 × 6 (for S atom)

 $+4 \times 6$  (for O atoms)

= 2 + 6 + 24

= 32 electrons.

A for PO4 ion

 $A = 1 \times 5$  (for P atom) +  $4 \times 6$  (for O atoms)

+ 3 (for charge)

= 5 + 24 + 3

= 32 electrons.

A for NH4 ion

 $A = 1 \times 5$  (for nitrogen atom) +  $4 \times 1$  (for H atoms)

- 1 (for positive charge)

= 5 + 4 - 1

= 8 electrons.

(iii) Calculate the total number of electrons needed by all atoms to achieve noble gas configuration. This number is represented by N.

For example: N for  $H_2SO_4$ 

$$N = 2 \times 2 + 8 \times 1 + 8 \times 4$$

= 4 + 8 + 32

= 44 electrons.

(iv) Calculate the total number of electrons shared. This is represented by S, which is equal to N-A.

For example: S for  $H_2SO_4$ 

S = N - A

= 44 - 32

= 12 electrons.

(v) Place the shared pair of electrons into the skeleton, using double and triple bonds only when necessary.

## for example:

Skeleton

Dot formula

Dash formula

(vi) Place the additional unshared (lone) pairs of electrons to fill the octet to every atom except hydrogen which can have only 2 electrons as the total comes equal to A as calculated in step (ii).

## For H<sub>2</sub>SO<sub>4</sub>

# SOME WORKED EXAMPLES

**Example 1.** Write the Lewis dot formula and dash formula for CO<sub>2</sub>.

**Solution:** Step (i) The skeleton is OCO.

Step (ii)

 $A = 1 \times 4$  (for C) + 2 × 6 (for O) = 4 + 12 = 16 electrons Step (iii)

 $N = 1 \times 8$  (for C) + 2 × 8 (for O) = 8 + 16 = 24 electrons Step (iv) S = N - A = 24 - 16 = 8 electrons shared

Step (v)

O::C::O

Step (vi) : O:: C:: O:

**Example 2.** Write the Lewis dot formula and dash formula for the  $SO_4^{2-}$  ion.

**Solution:** Step (i) The skeleton  $\begin{bmatrix} O \\ O S O \\ O \end{bmatrix}^{2-}$ 

Step (ii)

 $A = 1 \times 6$  (for S) +  $4 \times 6$  (for O) + 2 (for negative charge) = 6 + 24 + 2

= 32 electrons

Step (iii)

 $N = 1 \times 8 \text{ (for S)} + 4 \times 8 \text{ (for O)}$ 

= 8 + 32

= 40 electrons

Step (iv) S = N - A = 40 - 32 = 8 electrons shared

Step (v) 
$$O: S: O^{2-} O - S - O^{2-} O$$

**Example 3.** Write the Lewis dot formula or dash formula for the  $CO_3^2$  ion.

**Solution:** Step (i) Skeleton O C  $O^{2-}$ 

Step (ii)

 $A = 1 \times 4$  (for C) +  $3 \times 6$  (for O) + 2 (for negative charge)

= 4 + 18 + 2

= 24 electrons

Step (iii)

 $N = 1 \times 8$  (for C) +  $3 \times 8$  (for O)

= 8 + 24

= 32 electrons

Step (iv)

S = N - A

= 32 - 24

= 8 electrons shared (4 pairs shared)

Step (vi) 
$$: O: C:: O:^{2-}$$
 or  $: O - C = O^{2-}$ 

Electron dot formulae and Bond formulae of	or
Dash formulae of some compounds	

Molecular Formula	Electron dot Formula	Dash Formula or Bond Formula
(a) Compour	nds having electrovalent	bonds only
NaCl	Na <sup>+</sup> × Cl · -	Na <sup>+</sup> Cl <sup>-</sup>
MgCl <sub>2</sub>	Cl * Mg <sup>2+</sup> * Cl * -	Cl-Mg++Cl-
CaCl <sub>2</sub>	Cl * Ca <sup>2+</sup>	Cl <sup>-</sup> Ca <sup>++</sup> Cl <sup>-</sup>
MgO	$Mg^{2+} \stackrel{\circ}{\times} \stackrel{\circ}{O} \stackrel{\circ}{\bullet}^{2-}$	Mg <sup>++</sup> O <sup></sup>
Na <sub>2</sub> S	$Na^{+} \overset{\bullet}{\times} \overset{\bullet}{S} \overset{2-}{\times} Na^{+}$	Na <sup>+</sup> S <sup></sup> Na <sup>+</sup>
CaH <sub>2</sub>	$H \overset{\bullet}{\times} Ca^{2+} \overset{\bullet}{\times} H^{-}$	H <sup>-</sup> Ca <sup>++</sup> H <sup>-</sup>
AIF <sub>3</sub>	F * Al <sup>3+</sup> * F * -	F <sup>-</sup> Al <sup>3+</sup> F <sup>-</sup>
A) C		

# (b) Compounds having covalent bonds only

HCI	H & Cl	H—Cl
H <sub>2</sub> O	H * O * H	НОН
H <sub>2</sub> S	H * S * H	н—ѕ—н
NH <sub>3</sub>	H *• H * N * H	H   HN   H
HCN	H * C * N :	H—C≡N
CH <sub>4</sub>	H	H   HCH   H
C <sub>2</sub> H <sub>4</sub>	H H ו •× C × × C	Н Н     С=С

$$C_{2}H_{2} \qquad H \overset{\bullet}{\times} C \overset{\times}{\times} \overset{\times}{\times} C \overset{\bullet}{\times} H \qquad H-C \equiv C-H$$

$$C_{2}H_{6} \qquad H \overset{\bullet}{\times} C \overset{\times}{\times} C \overset{\bullet}{\times} H \qquad H-C-C-C-H$$

$$C_{2}H_{6} \qquad H \overset{\bullet}{\times} C \overset{\times}{\times} C \overset{\bullet}{\times} H \qquad H-C-C-C-H$$

$$H \overset{\bullet}{\times} H \qquad H \qquad H \qquad H$$

$$PH_{3} \qquad H \overset{\bullet}{\times} P \overset{\bullet}{\times} \qquad H \qquad H-P$$

$$C_{1} \overset{\bullet}{\times} C \overset{\bullet}{\times} C \overset{\bullet}{\times} H \qquad H-P$$

$$C_{1} \overset{\bullet}{\times} C \overset{\bullet}{\times} C \overset{\bullet}{\times} H \qquad H-P$$

$$C_{1} \overset{\bullet}{\times} C \overset{\bullet}{\times} C \overset{\bullet}{\times} C \overset{\bullet}{\times} H \qquad H-P$$

$$C_{1} \overset{\bullet}{\times} C \overset{\bullet}{\times} C \overset{\bullet}{\times} C \overset{\bullet}{\times} H \qquad H-P$$

## (c) Compounds having electrovalent and covalent bonds

NaOH 
$$Na^{+}\begin{bmatrix} \overset{.}{\circ} \overset{.}{\circ} \overset{.}{\circ} & H \end{bmatrix}^{-}$$
  $Na^{+}[O - H]^{-}$ 

KCN  $K^{+}\begin{bmatrix} \overset{.}{\circ} & \overset{.}{\circ} & \overset{.}{\circ} & 1 \end{bmatrix}^{-}$   $K^{+}[C = N]^{-}$ 

CaCO<sub>3</sub>  $Ca^{2+}\begin{bmatrix} \overset{.}{\circ} & \overset{.}{\circ} & \overset{.}{\circ} & \overset{.}{\circ} & 1 \end{bmatrix}^{2-}$ 

### (d) Compounds having covalent and coordinate bonds

Note: Remove proton from HNO<sub>3</sub> molecule.

Note: Remove proton from HNO2 molecule.

$$SO_2$$
  $\stackrel{\times}{\times} \stackrel{\circ}{O} : \stackrel{\circ}{S} : \stackrel{\times}{\times} \stackrel{\circ}{O} : \stackrel{\times}{\times} \stackrel{\circ}{O} : \stackrel{\circ}{\times} \stackrel{\circ}{\circ} \stackrel{\circ}{$ 

Note: On the basis of overlapping and hybridization concept, the structure of  $SO_2$  is,  $S_{i.e.}^{O}$ , i.e., octet rule is not followed.

Note: On the basis of overlapping and hybridization concept, the structure of  $SO_3$  is, O = S = O, *i.e.*, octet rule is not followed.

Note: Remove protons from H<sub>2</sub>SO<sub>4</sub> molecule.

Note: Remove protons from H<sub>2</sub>SO<sub>3</sub> molecule.

Note: For SO<sub>4</sub><sup>3</sup> remove protons from H<sub>3</sub>PO<sub>4</sub> molecule.

**Note**: For  $P_2O_7^{4-}$  remove protons from  $H_4P_2O_7$  molecule.

Note: Anhydrous aluminium chloride is a dimer.

Note: For IO<sub>3</sub> remove proton from HIO<sub>3</sub> molecule.

Note: For ClO<sub>4</sub> remove proton from HClO<sub>4</sub> molecule.

HClO<sub>3</sub> 
$$H \overset{\times \times}{\underset{\times}{\circ}} \overset{\circ}{\underset{\times}{\circ}} \overset{\circ}{\underset{\times}{\circ}} \overset{\times}{\underset{\times}{\circ}} \overset{\times}{\underset{\times}{\circ}} \times \overset{\times}{\underset{\times$$

Note: For ClO<sub>3</sub> remove proton from molecule.

# (e) Compounds having electrovalent, covalent and coordinate bonds

$$NH_4Cl \qquad \begin{bmatrix} H \\ \bullet \times \\ H \overset{\bullet}{\times} \overset{\bullet}{N} \overset{\bullet}{\bullet} H \end{bmatrix}^{+} \overset{\times \times}{\underset{\times \times}{\overset{\circ}{\circ}}} \begin{bmatrix} H \\ I \\ H - \overset{\bullet}{N} \longrightarrow H \end{bmatrix}^{+} Cl^{-}$$

 $K_4Fe(CN)_6$ 

**Isosters**: Molecules or ions (polyatomic) containing same number of atoms and the same total number of electrons are called isosters. Usually, isosters have same identical Lewis structures.

Isosteric species	No. of atoms	No. of electrons	Valency electrons
CH <sub>4</sub> , NH <sub>4</sub> <sup>†</sup>	5	10	(8)
CO <sub>2</sub> , N <sub>2</sub> O, CNO <sup>-</sup> , NO <sub>2</sub> <sup>+</sup>	3	22	(16)
$NO_3^-$ , $CO_3^{2-}$ , $BO_3^{3-}$	4	32	(24)
NH <sub>3</sub> , H <sub>3</sub> O <sup>+</sup>	4	10	(8)
ClO <sub>3</sub> , SO <sub>3</sub> <sup>2-</sup>	4	42	(26)
$ClO_4^-$ , $PO_4^{3-}$	5	50	(32)
$MnO_4^-$ , $CrO_4^{2-}$	5	58	(32)

N<sub>2</sub>, CO and CN<sup>-</sup> are isosters. Their Lewis structures are identical.

$$\stackrel{\times}{\times}$$
  $\stackrel{\times}{\times}$   $\stackrel{\times}$ 

# 2.22 FORMAL CHARGE

In case of the polyatomic ions, the net charge is possessed by an ion as a whole and not by a particular atom. However, for some purposes each atom in a polyatomic ion or molecule is assigned a **formal charge**. It is defined as the difference between the number of valence electrons in an isolated (*i.e.*, free) atom and the number of electrons assigned to that atom in a Lewis structure. The counting of electrons is based on the assumption that the atom in the molecule owns one electron of each shared pair and both the electrons of a lone pair.

Formal charge on an atom = total number of valence electrons in the free atom - total number of non bonding (lone pair) electrons -  $\frac{1}{2}$  total number of bonding (shared) electrons

The concept of formal charge can be explained by nitrous oxide molecule,  $N_2O$ . The electron dot structure for  $N_2O$  can be written as :

Using the given relationship, the formal charges on the three atoms can be calculated as follows:

## (a) Terminal nitrogen atom:

Valence electrons = 5

Lone pair = one (two electrons)

Total number of bonding electrons = 6

Formal charge 
$$= 5 - 2 - \frac{1}{2} \times 6 = 0$$

#### (b) Central nitrogen atom:

Valence electrons = 5

Lone pair = nil

Total number of bonding electrons = 8

Formal charge =  $5 - \frac{1}{2} \times 8 = +1$ 

#### (c) Terminal oxygen atom:

Valence electrons = 6

Lone pair = three (six electrons)

Total number of

bonding electrons = 2

Formal charge = 
$$6 - 6 - \frac{1}{2} \times 2 = -1$$

Thus, the structure can be written as follows:

The advantage of calculation of formal charges is that it helps to select the most stable structure of the molecule or ion. The most stable structure is the one which has the smallest formal charges on the atoms or zero formal charges on the atoms. Negative formal charges should appear on the most electronegative atoms. Adjacent atoms in the structure should not carry the formal charges of same sign. The total formal charges on the atoms in a Lewis structure must be zero for a neutral molecule and must equal to net charge for a polyatomic ion.

**Example 4.** Calculate the formal charges on atoms in (a)  $CS_2$  and (b)  $CO_3^{2-}$  ion

Solution: (a) Lewis structure of CS<sub>2</sub> is

$$\dot{S} = C = \dot{S}$$

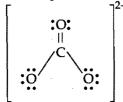
Formal charge on each sulphur atom = valence electrons – lone pair electrons – (1/2) bonding electrons

$$=6-4-(1/2)\times 4=0$$

Formal charge on carbon atom = valence electrons – lone pair electrons – 1/2 bonding electrons

$$= 4 - 0 - (1/2) \times 8 = 0$$

(b) Lewis structure of  $CO_3^{2-}$  ion is



Formal charge on carbon atom =  $4 - (1/2) \times 8 = 0$ Formal charge on double bonded O atom

$$=6-4-(1/2)\times 4=0$$

Formal charge on single bonded O atom

$$= 6 - 6 - (1/2) \times 2 = -1$$

**Example 5.** Select the most stable correct structure of COCl<sub>2</sub>

**Solution :** (a) FC on O atom =  $6 - 6 - (1/2) \times 2 = -1$ 

FC on C atom =  $4 - 0 - (1/2) \times 8 = 0$ 

FC on Cl atom =  $7 - 6 - (1/2) \times 2 = 0$ 

FC on Cl atom =  $7 - 4 - (1/2) \times 4 = +1$ 

(b) FC on C atom =  $4 - 4 - (1/2) \times 4 = -2$ 

FC on O atom =  $6 - 0 - (1/2) \times 8 = +2$ 

FC on Cl atom =  $7 - 6 - (1/2) \times 2 = 0$ 

(c) FC on O atom =  $6 - 4 - (1/2) \times 4 = 0$ 

FC on C atom =  $4 - 0 - (1/2) \times 8 = 0$ 

FC on Cl atom =  $7 - 6 - (1/2) \times 2 = 0$ 

Structure (c) with formal charges of zero is the most stable correct structure.

# 2.23 POLARITY OF COVALENT BOND

In all homonuclear diatomic molecules like hydrogen molecule  $(H_2)$ , chlorine molecule  $(Cl_2)$ , fluorine molecule  $(F_2)$ , oxygen molecule  $(O_2)$ , the electron pair or pairs is shared equally between the two atoms. This means that shared electrons are equally attracted to both the nuclei and therefore spend equal amounts of time near each nucleus. As a result, the molecule is **neutral** or **non-polar**.

When the heteronuclear diatomic molecule is considered the situation is not simple. Electronegativity is defined as the tendency of an atom to attract electrons towards itself in a chemical bond. Thus, in heteronuclear diatomic molecule, both the atoms joined by the covalent bond possess different electronegativity. As a result, the atom having higher value of electronegativity attracts the shared electron pair much more strongly than the other atom. For example, in HF the electron pair is more attracted towards F as it is more electronegative than hydrogen. Due to this, the fluorine end of the molecule appears negative and the hydrogen end positive. Such molecules having two oppositely charged poles are called polar molecules and the bond is said to be a polar covalent bond.

A covalent bond, in which electrons are shared unequally and the bonded atoms acquire a partial positive and negative charge, is called a polar covalent bond or a covalent bond between two dissimilar atoms is a polar covalent bond.

Two kinds of notation are used to indicate a polar covalent bond.

Polar covalent bonds may be thought of as being intermediate between the non-polar bonds and pure ionic bonds.

Bond polarity is described in terms of ionic character which usually increases with increasing difference in the electronegativity (EN) between bonded atoms.

Ionic character decreases as the difference in electronegativity decreases

Pauling has estimated the approximate percentage of ionic character in various A—B covalent bonds from the ( $X_A$  –  $X_B$ ) values, *i.e.*, electronegativity difference of the two atoms forming the covalent bond.

$X_A - X_B$		Percentage of ionic character	Nature of A—B bond
	0	0	Purely covalent
	0.1 to 0.8	0.5 - 15	Covalent
	0.9 to 1.8	19 - 47	Polar covalent
	1.9	50	50% ionic and 50% covalent
	2 to 3.2	55-93	Ionic

Hanny and Smyth gave the following equation for calculating the percentage of ionic character in A—B bond on the basis of the values of electronegativity of the atoms A and B. Percentage of ionic character =  $[16(X_A - X_B) + 3.5(X_A - X_B)^2]$ 

This equation gives approximate calculation of percentage of ionic character, *e.g.*, 50% ionic character corresponds to  $(X_A \sim X_B)$  equal to 2.1.

**Example 6.** Calculate the percentage of ionic character in Cs—Cl bond in CsCl molecule. The electronegativity values of Cs and Cl are 0.7 and 3.0 respectively.

**Solution :** 
$$X_A - X_B = X_{CI} - X_{Cs} = (3.0 - 0.7) = 2.3$$
  
Percentage of ionic character in Cs—Cl bond  
=  $[16 \times 2.3 + 3.5 \times (2.3)^2]$   
=  $[36.8 + 18.51]$   
=  $55.31$ 

**Example 7.** Arrange molecules HF, HCl, HBr and HI in the decreasing order of the percentage of ionic character. Electronegativity values are as follows:

$$H = 2.1$$
,  $F = 4.0$ ,  $Cl = 3.0$ ,  $Br = 2.8$ ,  $I = 2.5$   
Solution: Percentage of ionic character in H—F  
 $= [16 \times 1.9 + 3.5 \times (1.9)^2]$   
 $= 43$   
% ionic character in H—Cl =  $[16 \times 0.9 + 3.5 \times (0.9)^2]$   
 $= 17.2$   
% ionic character in HBr =  $[16 \times 0.7 + 3.5 \times (0.7)^2]$   
 $= 12.9$   
% ionic character in HI =  $[16 \times 0.4 + 3.5 \times (0.4)^2]$   
 $= 7.0$   
Order HF > HCl > HBr > HI

# 2.24 DIPOLE MOMENT

Difference in polarities of bonds is expressed on a numerical scale. The polarity of a molecule is indicated in terms of **dipole moment** ( $\mu$ ). To measure dipole moment, a sample of the substance is placed between two electrically charged plates. Polar molecules orient themselves in the electric field causing the measured voltage between the plates to change.

The dipole moment is defined as the product of the distance separating charges of equal magnitude and opposite sign, with the magnitude of the charge. The distance between the positive and negative centres is called the bond length. Thus,

$$\mu = \text{electric charge} \times \text{bond length}$$

$$= q \times d$$

As q is in the order of  $10^{-10}$  esu and d is in the order of  $10^{-8}$  cm,  $\mu$  is in the order of  $10^{-18}$  esu cm. Dipole moment is measured in 'Debye' unit (D).

$$1 D = 10^{-18}$$
 esu cm =  $3.33 \times 10^{-30}$  coulomb metre

Generally, as electronegativity difference increases in diatomic molecules, the value of dipole moment increases. Greater the value of dipole moment of a molecule, greater the polarity of the bond between the atoms.

Molecule	HI	H-Br	H—C1	H-F
% ionic character	7	12.9	17.2	43
$(X_A - X_B)$	0.4	0.7	0.9	1.9
Dipole moment-	0.38 D	0.78 D	1.03 D	1.92 D

Dipole moment is a vector quantity, *i.e.*, it has both magnitude as well as direction. The overall value of the dipole moment of a polar molecule depends on its geometry and shape, *i.e.*, vectorial addition of dipole moment of the constituent bonds. A symmetrical molecule is non-polar even though it contains polar bonds. For example, CO<sub>2</sub>, BF<sub>3</sub>, CH<sub>4</sub>, CCl<sub>4</sub> being symmetrical molecules have zero resultant dipole moments and hence are non-polar since dipole moments summation of all the bonds present in the molecule cancel each other. Dipole moment is usually indicated by an arrow having + on the tail (+—), above the polar bond and pointing towards the negative end.

$$0 \stackrel{\longleftarrow}{=} C \stackrel{\longleftarrow}{=} 0 \qquad \qquad \downarrow \\ F \stackrel{\longrightarrow}{=} B \qquad \qquad \downarrow \\ F \stackrel{\longleftarrow}{=} C \stackrel{\longleftarrow}{\longrightarrow} H$$

Unsymmetrical non-linear polyatomic molecules always have net value of dipole moment, thus such molecules are polar in nature. H<sub>2</sub>O, CH<sub>3</sub>Cl, NH<sub>3</sub>, etc., are polar molecules as they have some positive values of dipole moments.

$$H = 0$$

$$H = 1.84D$$

$$Water \mu = 1.84D$$

$$Cl$$

$$H = 1.60D$$

$$H = 1.60D$$

$$H = 1.60D$$

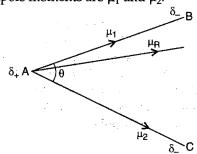
$$H = 1.60D$$

$$H = 1.46D$$

$$H = 1.46D$$

# **■** Calculation of Resultant Bond Moments

Let AB and AC are two polar bonds inclined at an angle  $\theta$ , their dipole moments are  $\mu_1$  and  $\mu_2$ .



Resultant dipole moment may be calculated using vectorial method.

$$\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

when,  $\theta = 0$ , the resultant is maximum.

$$\mu_R = \mu_1 + \mu_2$$
when,  $\theta = 180^\circ$ , the resultant is minimum.

 $\mu_R = \mu_1 \sim \mu_2$ 

#### **DIPOLE MOMENT OF SOME COMMON SUBSTANCES**

Compound	Dipole moment (D)	Compound	Dipole moment (D)	Compound	Dipole moment (D)
HF	1.92	NH <sub>3</sub>	1.46	CH <sub>3</sub> Cl	1.86
HCl	1.03	H <sub>2</sub> O	1.84	C <sub>2</sub> H <sub>5</sub> OH	1.68
HBr	0.78	H <sub>2</sub> S	0.92	CH <sub>3</sub> COCH <sub>3</sub>	1.30
HI	0.38	SO <sub>2</sub>	1.60	C <sub>6</sub> H <sub>5</sub> Cl	1.57

# **■** Applications of Dipole Moment

- (i) To decide polarity of the molecule: Molecules having zero dipole moment\* are said to be non-polar molecules and those having  $\mu_R \neq 0$  are polar in nature.
- (ii) To determine percentage of ionic character: The value of dipole moment can be used for determining the amount of ionic character in a bond. Consider a diatomic molecules say HCl. Suppose this molecule is completely ionic. Under this condition  $H^+$  and  $Cl^-$  ions would bear a unit charge equal to  $4.8 \times 10^{-10}$  esu and the bond distance between H and Cl atoms = 1.27 Å.

Thus, theoretical value of  $\mu$  (considering molecule completely ionic)

$$= 4.8 \times 10^{-10} \times 1.27 \times 10^{-8} = 6.09 \text{ D}$$

Dipole moment of HCl is also determined experimentally. Let the experimental value be 1.03 D.

Percentage of ionic character in H—Cl bond in HCl molecule

= Experimental value of 
$$\mu$$
  
Theoretical value of  $\mu$  × 100 =  $\frac{1.03}{6.09}$  × 100 = 16.9

Thus, percentage of ionic character

Experimental value of dipole moment

- Theoretical value of dipole moment × 100
- (iii) To determine geometry of molecules: The values of dipole moments provide valuable information about the structure of molecules.
- (a)  $CO_2$ ,  $CS_2$  molecules are linear as values of their dipole moments are zero.
- (b)  $H_2O$  is not a linear molecule as it has dipole moment. Actually, it has V-shaped structure and the bond angle is  $105^\circ$ . Similarly,  $SO_2$  has a bent structure.
- (c) In ammonia, three hydrogen atoms do not lie symmetrically with respect to nitrogen as it has dipole moment. It has pyramidal structure.

#### MOLECULAR GEOMETRY AND DIPOLE MOMENT

General formula	Molecular geometry	Dipole moment	Example
$\overline{AX}$	Linear	May be non-zero	HF, HCl
$AX_2$	Linear	Zero	CO <sub>2</sub> ,CS <sub>2</sub>
	Bent or V-shape	Non-zero	$H_2O$ , $NO_2$
$AX_3$	Triangular planar	Zero	BF <sub>3</sub>
	Pyramidal	Non-zero	NH <sub>3</sub> , PCl <sub>3</sub>
	T-shape	Non-zero	ClF <sub>3</sub>
$AX_4$	Tetrahedral	Zero	CH <sub>4</sub> , CCl <sub>4</sub>
	Square planar	Zero	XeF <sub>4</sub>
	See-saw	Non-zero	SF <sub>4</sub> , TeCl <sub>4</sub>
$AX_5$	Trigonal bipyramidal	Zero	PCl <sub>5</sub>
	Square pyramidal	Non-zero	BrCl <sub>5</sub>
$AX_6$	Octahedral	Zero	SF <sub>6</sub>
	Distorted octahedral	Non-zero	XeF <sub>6</sub>
$AX_7$	Pentagonal bipyramidal	Zero	IF <sub>7</sub>

(iv) To distinguish *cis* and *trans* forms of geometrical isomers: Experimental values of dipole moment of the isomers (*cis* and *trans*) are determined. The *trans* isomer usually possesses either zero dipole moment or very low value in comparison to *cis* form.

It should be noted that if two groups have opposite inductive character then *trans* isomer will have greater dipole moment of,

H Cl Cl H

C H

C CH<sub>3</sub> H

Trans

$$CH_3$$
 H

 $CH_3$  H

 $CH_3$  H

 $CH_3$  H

(v) To determine orientation in benzene ring: Dipole moment is useful to ascertain the orientation of substituents. The greater the dipole moment, the greater is the asymmetry. In general, dipole moment follows the order:

<sup>\*</sup>In the symmetrical molecules having polar bonds, centre of positive and negative poles coincides leading to zero dipole moment.

In ortho isomers, experimental value of dipole moment is found different from theoretical value of dipole moment. This difference is due to dipole-dipole interaction of two groups.

(vi) Bond moment: The contribution of individual bond in the dipole moment of a polyatomic molecule is termed bond moment. The measured dipole moment of water molecule is 1.85 D. This dipole moment is the vectorial sum of the individual bond moments of two O—H bonds having bond angle 104.5°.

Thus, 
$$\mu_{\text{obs}} = 2\mu_{\text{O}}$$
 cos 52.25  
or  $1.85 = 2\mu_{\text{O}}$  × 0.6129  
 $\mu_{\text{O}}$  = 1.51 D

#### Conclusions

- (i) Dipole moment ∞ Electronegativity difference For example, HF > HCl > HBr > HI
- (ii) Dipole moment 

  Number of lone pairs of electrons
  For example, HF > H<sub>2</sub>O > NH<sub>3</sub>

  Fluorine has 3 lone pairs, oxygen has 2 lone pairs
  and nitrogen has one lone pair.
- (iii) Dipole moment  $\propto 1/\theta$

X X 60° 120° 180°

(iv) Homoatomic molecules and molecules having normal shapes such as linear, trigonal, tetrahedral possess zero dipole moment.

For example, Cl<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, BCl<sub>3</sub>, CCl<sub>4</sub>, SiCl<sub>4</sub>

- (v) Molecules having distorted shapes like angular, pyramidal, sea-saw, etc, show dipole moments. For example, H<sub>2</sub>O, SO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, SF<sub>4</sub>
- (vi) Dipole moment of a cis-alkene is more than transalkene. In trans-alkenes, it is zero due to similar groups (symmetry).
  It should be noted that if two groups have opposite inductive character, then trans isomer will have

greater dipole moment.

# 2/25 POLARISATION (CHANGE OF IONIC CHARACTER TO COVALENT CHARACTER)

When two oppositely charged ions of unequal size approach each other closely (during formation of an electrovalent bond), the ion smaller in size attracts outermost electrons of the other ion and repel its nuclear charge. The net result is distortion or polarisation of the bigger ion. This distortion is usually done by the cation as its size is smaller than the anion. The electron cloud of anion no longer remains symmetrical but is elongated towards the cation. The ability of a cation to polarise the nearby anion is called its **polarising power** and the tendency of an anion to get distorted or

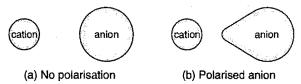


Fig. 2.6 Representation of Polarisation

deformed or polarised by the cation is called its **polarisability**. Due to polarisation, sharing of electrons occur between two ions to some extent and the bond shows some covalent character. This is shown in Fig.2.6.

The magnitude of polarisation depends upon a number of factors or the increased covalent character is favoured by a number of factors. These factors were suggested by Fajan and are known as Fajan's rules.

(i) Charge on cation: As the charge on the cation increases, its tendency to polarise the anion increases. This brings more and more covalent nature in the electrovalent compound.

For example, in the case of NaCl, MgCl<sub>2</sub> and AlCl<sub>3</sub> the polarisation increases, thereby covalent character becomes more and more as the charge on the cation increases.

Cation	Cation charge	Formula of the chloride	Melting point of t chloride, °C	
Na <sup>+</sup>	+1	NaCl	800	Covalent
Mg <sup>++</sup>	+2	MgCl <sub>2</sub>	712	character
$Al^{+++}$	+3	AlCl <sub>3</sub>	Sublimes	increases

Similarly, lead forms two chlorides  $PbCl_2$  and  $PbCl_4$  having charges +2 and +4 respectively.  $PbCl_4$  shows covalent nature.

In general, if a metal forms more than one halide, the halide having higher charge on the cation (i.e., higher oxidation state) is usually more covalent in nature in comparison to halide having a cation with lower charge, i.e., lower oxidation state or in other words, the melting point of the halide having higher oxidation state is less than the melting point of halide having lower oxidation state.

(ii) Size of the cation: Polarisation of the anion increases as the size of the cation decreases, *i.e.*, the electrovalent compounds having smaller cations show more of the covalent nature. For example, in the case of halides of alkaline earth metals, the covalent character decreases.

Cation	Radius of the cation Å	Formula of the chloride	Melting point of the chloride, °C	
Be <sup>2+</sup>	0.31	BeCl <sub>2</sub>	405	t te
$Mg^{2+}$ $Ca^{2+}$	0.65	MgCl <sub>2</sub>	712	ent ter ses point
	0.99	CaCl <sub>2</sub>	772	Covalent character increases increases slting po
Sr <sup>2+</sup>	1.13	SrCl <sub>2</sub>	872	getti ji g C
Ba <sup>2+</sup>	1.35	BaCl <sub>2</sub>	960	2

Low melting point indicates more covalent nature.

(iii) Size of anion: The larger the size of the anion, more easily it will be polarised by the cation, *i.e.*, as the size of the anion increases for a given cation, the covalent character increases. For example, in the case of halides of calcium, the covalent character increases from  $F^-$  anion to  $I^-$  anion.

Cation	Anion	Anion size Å	Formula of the halide	Melt	ing point of the halide, °C
Ca <sup>2+</sup>	F-	1.36	CaF <sub>2</sub>	1932	nt ss ss oint
	Cl <sup>-</sup>	1.81	CaCl <sub>2</sub>	772	alent racter eases ng poi
	Br <sup></sup>	1.95	CaBr <sub>2</sub>	730	Cov Shar incre settin
	I-	2.16	CaI <sub>2</sub>	575	Ţ , "ŢŞ ,

Similarly, in the case of trihalides of aluminium, the covalent character increases with increase in size of halide anion.

(iv) Configuration of cation: The cations with 18 electrons in outermost shell bring greater polarisation of the anion than those with inert gas configuration even if both the cations have same size and same charge. For example, CuCl is more covalent than NaCl.

Cu <sup>+</sup> Ion	2, 8, 18	Na <sup>+</sup> 2, 8
Size	0.96 Å	0.95 Å
Malima maint	C-C1 4429C	NI-C1 000

Melting point CuCl, 442°C NaCl, 800°C Cations having more of core electrons are more

Cations having more of core electrons are more polarising and thus, favour covalency.

In general, all those electrovalent compounds having high values of polarisation (more covalent character) are found to be less soluble in water but more soluble in organic solvents. The following examples support this view:

- (i) Sulphides are less soluble in water than oxides of the same metal.
  - (ii) Lithium salts are soluble in organic solvents.
- (iii) Beryllium compounds are less soluble than corresponding other alkaline earth metal compounds.
- (iv) The solubility of aluminium halides decreases from AlF<sub>3</sub> to AlI<sub>3</sub>.

# Points to Remember

- (i) On moving down a group, the polarising power of the cations goes on decreasing.
- (ii) Polarising power of the cations increase in moving left to right in a period.
- (iii) The polarisability of the anions by a given cation decreases in moving left to right in a period.
- (iv) The polarisability of the anions by a given cation increases moving down a group.
- (v) Increase of polarisation brings more of covalent character in an ionic compound. The increased covalent character is indicated by the decrease in melting point of the ionic compound. Examples:

Polarisation increases →
Covalent character increases →

Melting point decreases -----

(a) NaF < NaCl < NaBr < NaI (Size of anion increases) m.pt. (°C) 988 801 755 651 (b) CaF
$$_2$$
 < CaCl $_2$  < CaBr $_2$  < CaI $_2$  (Size of anion increases) m.pt. (°C) 1392 772 730 575 (c) BaCl $_2$  < SrCl $_2$  < CaCl $_2$  < MgCl $_2$  < BeCl $_2$  (Size of cation decreases) m.pt. (°C) 960 872 772 712 405 (d) NaCl < MgCl $_2$  < AlCl $_3$  (Charge on the cation increases)

(e) LiCl 
$$<$$
 BeCl $_2$   $<$  BCl $_3$   $<$  CCl $_4$  (Size of the cation decreases)

sublimes

(f) 
$$GeCl_2 < GeCl_4$$
;  $SnCl_2 < SnCl_4$ ;  $PbCl_2 < PbCl_4$ 

(g) 
$$HF < H_2O < NH_3 < CH_4$$

(i) NaCl < CuCl; NaI < AgI

m.pt. (°C) 801

# 2.26 HYDROGEN BONDING

In 1920, **Latimer** and **Rodebush** introduced the idea of "hydrogen bond" to explain the nature of association in liquid state of substances like water, hydrogen fluoride, ammonia, formic acid, etc. In a hydrogen compound, when hydrogen is bonded to highly electronegative atom (such as F, O, N) by a covalent bond, the electron pair is attracted towards electronegative atom so strongly that a dipole results, *i.e.*, one end carries a positive charge (H–end) and other end carries a negative charge (X–end).

If a number of such molecules are brought nearer to each other, the positive end of one molecule and negative end of the other molecule will attract each other and weak electrostatic force will develop. Thus, these molecules will associate together to form a cluster of molecules.

The attractive force that binds hydrogen atom of one molecule with electronegative atom of the other molecule of the same or different substance is known as **hydrogen bond**. This bond is represented by 3 dotted line.

Hydrogen bonding is of two types.

(a) Intermolecular hydrogen bonding: This type of bonding results between the positive and negative ends of different molecules of the same or different substances.

## Examples 8.

#### (i) Hydrofluoric acid:

#### (ii) Ammonia:

#### (iii) Water:

(iv) Formic acid:

#### (v) p-chlorophenol:

$$--\frac{\delta_{-}}{Cl} \longrightarrow O-H--Cl \longrightarrow O-H--Cl$$

$$\longrightarrow O-H--Cl$$

$$\longrightarrow O-H--Cl$$

This type of hydrogen bonding increases the boiling point of the compound and also its solubility in water. The increase in boiling point is due to association of several molecules of the compound.

Intermolecular hydrogen bond is also responsible for increase in the viscosity. Greater is the extent of hydrogen bonding more is the viscosity.

C.P. stands for centipoise.

(b) Intramolecular hydrogen bonding: This type of bonding results between hydrogen and an electronegative element both present in the same molecule. This type of bonding is generally present in organic compounds. Examples are *o*-chlorophenol, *o*-nitrophenol, *o*-hydroxy benzoic acid, etc.

This type of bonding decreases the boiling point of the compound. The solubility of the compound also decreases.

# ■ Nature and Importance of Hydrogen Bond

- (i) Hydrogen bond is merely an electrostatic force rather than a chemical bond.
  - (ii) Hydrogen bond never involves more than two atoms.
- (iii) Bond energy of hydrogen bond is in the range of 3 to 10 kcal/mole (10 to 40 kJ per mole), *i.e.*, about 1/10 the energy of a covalent bond (strength 50–100 kcal mol<sup>-1</sup>).
- (iv) With the increase of electronegativity and decrease in size of the atom to which hydrogen is covalently linked, the strength of the hydrogen bond increases. It is evident from the energies of hydrogen bonds in the three elements.

$$H - F - - - H > H - O - - - H > H - N - - - H$$
10 kcal mol<sup>-1</sup>
7 kcal mol<sup>-1</sup>
2 kcal mol<sup>-1</sup>

Energy of some hydrogen bonds in neutral molecules are tabulated below:

Bond	Average bond energy kJ mol <sup>-1</sup>
F—HO	40–45
F—HF	2325
O-H-O	20–30
OHS	15–20
OHF	12–15
NHN	12–25
NHO	20–25

(v) All the three atoms in X—H- - - X lie in the straight line.

Without hydrogen bonding water would have existed as a gas like hydrogen sulphide. In that case, no life would have been possible on this earth. Hydrogen bonding exists in molecules of living organisms. It exists in various tissues, blood, skin, bones, etc. The cotton, silk or synthetic fibres possess rigidity and tensile strength due to hydrogen bonding. The stickiness of glue or honey is also due to hydrogen bonding. Thus, hydrogen bonding has great importance in everyday life.

# ■ Properties Explained by Hydrogen Bonding

- (a) High boiling and melting points of  $NH_3$ ,  $H_2O$  and HF in comparison to hydrides of other elements of V, VI and VII groups to which N,O and F belong, respectively, are due to hydrogen bonding.  $H_2O$  exists in liquid state under ordinary condition while  $H_2S$  in gaseous state as hydrogen bonding exists in water and no hydrogen bonding exists in  $H_2S$ .
- (b) Unique properties of water and ice are due to hydrogen bonding. Density of ice is less than water and water contracts when heated between 0°C to 4°C. These two unique properties are on account of open cage structure of ice due to hydrogen bonding.
- (c) Strength of certain acids and bases can be explained on the basis of hydrogen bonding.
- (d) Solubility: A substance is said to be insoluble in water if it does not form hydrogen bonding with water. The organic compound like alkanes, alkenes, ethers, etc., are insoluble in water as they do not form hydrogen bonding with water, while alcohols and acids are soluble because they readily form hydrogen bonds with water.

Note: Chlorine has the same electronegativity as nitrogen but does not form strong hydrogen bonds. This is because of the larger size than that of nitrogen with the result that its electrostatic attractions are weak.

# 2.27 MODERN CONCEPT OF COVALENT BOND

The Lewis or octet concept does not explain the following points:

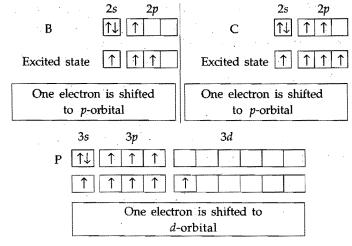
- (i) The cause of covalent bond formation.
- (ii) Nature of the forces operating between the atoms forming a covalent bond.
- (iii) Why different amounts of energies released during the formation of different molecules.
  - (iv) Shape and geometry of molecules.
- (v) Why the molecules are stable in which central atoms have either less than 8 electrons or more than 8 electrons in the outermost shell.

To explain the above limitations, the following two theories based on quantum mechanics have been proposed.

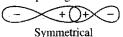
- (a) The valence bond theory and
- (b) Molecular orbital theory.

The valence bond theory: This theory was presented by Heitler and London, in 1927, to explain how a covalent bond is formed. This theory was extended by Pauling and Slater, in 1931. The main points of the theory are:

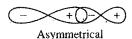
- (i) A covalent bond is formed by overlapping of atomic orbitals of valency shell of the two atoms\*.
- (ii) Only half filled atomic orbitals, *i.e.*, orbitals singly occupied can enter into overlapping process. The resulting bond acquires a pair of electrons with opposite spins.
- (iii) The atoms with half filled orbitals must come closer to one another with their axes in proper directions for overlapping.
- (iv) As a result of overlapping, there is maximum electron density somewhere between the two atoms. A large part of bonding force comes into existence from the electrostatic attraction between the nuclei and the accumulated electron cloud between them.
- (v) Greater the overlapping, higher is the strength of the chemical bond. The amount of energy released per mole during overlapping is termed bond energy. This energy stabilises the system. Hence, the molecule formed has less energy and consequently more stability than the isolated atoms.
- (vi) Electrons which are already paired in valency shell can enter into bond formation if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same main energy shell (valency shell). This point explains the trivalency of boron, tetravalency of carbon, pentavalency of phosphorus, hexavalency of sulphur and heptavalency of halogens (Cl, Br, I) inspite of the fact that these atoms have paired orbital or orbitals in the valency shell.



\*Only symmetrical overlap bring out the covalent bond formation, e.g.,







(vii) Between two orbitals of the same stability (i.e., having same energy) one more directionally concentrated would form a stronger bond. Dumb-bell shaped *p*-orbitals will form stronger bond as compared to spherically symmetrical s-orbital. It is formed by head on or axial overlap.

(viii) Two types of bonds are formed on account of overlapping. These are (a) Sigma ( $\sigma$ ) and (b) Pi ( $\pi$ ) bonds.

# 麗 (a) Sigma (σ) Bond

A bond formed between two atoms by the overlap of singly occupied orbitals along their axes (end to end overlap) is called **sigma** ( $\sigma$ ) **bond**. In such a bond formation, maximum overlap is possible between electron clouds and hence, it is a strong bond. Electron cloud of this bond is symmetrical about the line joining the two nuclei of the two atoms. Sigma bond can, thus, be defined as:

"Bond orbital which is symmetrical about the line joining the two nuclei is known as sigma bond." It is formed by head on or axial overlap.

Sigma bonds are formed by three types of overlapping:

(i) s-s overlapping (Formation of hydrogen molecule): Each hydrogen atom has one electron in 1s-orbital which is spherical. 1s-orbital of both the hydrogen atoms approach each other closely and when they reach a point of maximum attraction by the two nuclei, they overlap and form a sigma bond.

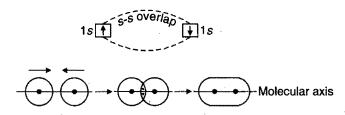


Fig. 2.7 Formation of H<sub>2</sub> molecule by s-s overlapping

The bond has two electrons which have opposite spins. The probability of finding these electrons is maximum in the region between the two nuclei on the molecular axis. The electron density of the bond is distributed symmetrically about the molecular axis.

- (ii) s-p overlapping (Formation of HF, H<sub>2</sub>O, NH<sub>3</sub> molecules) :
- (a) Formation of HF molecule: In the formation of HF molecule the 1s-orbital of hydrogen overlaps with the positial of fluorine containing unpaired electron.

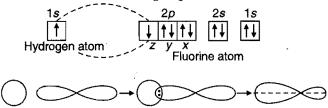


Fig. 2.8 Formation of HF molecule by s-p overlapping

**(b)** Formation of water molecule: Oxygen atom has the configuration of valency shell  $1s^2 2p_z^2 p_y^1 p_x^1$ , *i.e.*, it has two orbitals singly occupied. These two orbitals overlap with 1s-orbital of two hydrogen atoms forming sigma bonds.

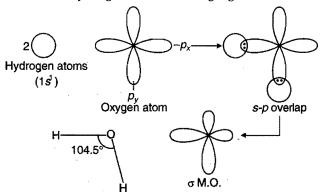


Fig. 2.9 Formation of water molecule by s-p overlapping

Since the two orbitals of oxygen are at right angle to each other an angle of 90° is expected between two sigma bonds but actual bond angle observed is 104.5°.

(c) Formation of ammonia molecule: Nitrogen atom has the configuration of valency shell  $2s^2 2p_x^1 2p_y^1 2p_z^1$ , *i.e.*, three singly occupied orbitals are present. These orbitals overlap with 1s-orbitals of three hydrogen atoms forming three sigma bonds.

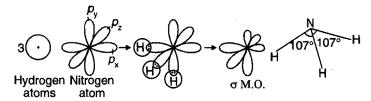


Fig. 2.10 Formation of NH3 molecule by s-p overlapping

Since the three orbitals of nitrogen are at right angle to each other, the expected angle between two sigma bonds should be 90 but actual bond angle observed is 107°.

(iii) p-p overlapping (Formation of fluorine molecule): This is illustrated by the formation of fluorine molecule. The electronic configuration of fluorine atom is  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$ , *i.e.*, one orbital is singly occupied. When p-orbitals of two fluorine atoms approach each other with their heads directly towards one another, they overlap and form a sigma bond.

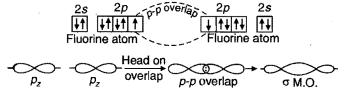


Fig. 2.11 Formation of F2 molecule by p-p overlapping

**Note :** Strongness of overlapping follows the following order : p-p > s-p > s-s

# 🗟 (b) Pi (π) Bond

 $\pi$ -bonds are formed by the sidewise or lateral overlapping of p-orbitals. The overlapping takes place at the side of two lobes and hence, the extent of overlapping is relatively smaller. Thus,  $\pi$ -bond is a weaker bond in comparison to sigma bond. The molecular orbital is oriented above and below the plane containing nuclear axis.

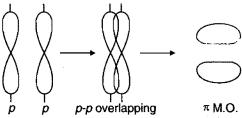


Fig. 2.12 Formation of  $\pi$ -bond

**Formation of oxygen molecule :** Oxygen atom has two p-orbitals singly occupied in the valency shell. When two oxygen atoms approach each other, one set of p-orbitals experiences head on overlap forming a sigma bond while other set of p-orbitals overlaps sidewise to form a  $\pi$ -bond. Thus, oxygen molecule has one  $\sigma$ - and one  $\pi$ -bond.

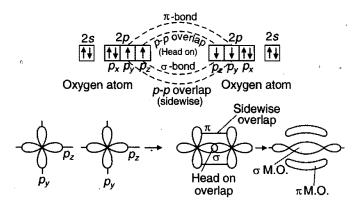


Fig. 2.13 Formation of O2 molecule

Similarly, the formation of nitrogen molecule can be explained. It has one sigma bond and two  $\pi$ -bonds.

## COMPARISON OF SIGMA ( $\sigma$ ) AND PI ( $\pi$ ) BOND

	Sigma bond	Pi bond
1.	•	
2.	It is a strong bond.	It is a weak bond.
3.	Electron cloud is symmetrical about the line joining the two nuclei.	Electron cloud is unsymmetrical.
4.	There can be free rotation of atoms around this bond.	Free rotation is not possible around this bond.
5.	These are less reactive.	These are more reactive.

6. The shape of the molecule is	These bonds do not affect the
determined by these bonds.	shape of the molecule.
<ol> <li>σ-electrons are referred as localized.</li> </ol>	$\pi$ -electrons are referred as mobile electrons.
8. σ-bond can have independent existence.	$\pi\text{-bond}$ always exists along with a $\sigma\text{-bond}.$

All single bonds are sigma bonds. A double bond consists of one sigma and one  $\pi$ -bond while a triple bond consists of one sigma and two  $\pi$ -bonds.

(i) **Bond energy** increases from a single bond to a triple bond.

Bond energy: Single bond < Double bond < Triple bond (ii) **Bond** strength increases from a single bond to a triple bond.

Bond strength: Single bond < Double bond < Triple bond (iii) **Bond length** of a multiple bond (double or triple) is always shorter than the corresponding single bond.

. Bond length: Single bond > Double bond > Triple bond

(iv) **Reactivity** of a multiple bond is always more than the single bond. This is due to the fact that  $\pi$ -electrons are mobile in nature.

Reactivity: Single bond < Double bond < Triple bond.

# 2.28 HYBRIDIZATION

The valence bond theory (overlapping concept) explains satisfactorily the formation of various molecules but it fails to account the geometry and shapes of various molecules. 31 does not give explanation why BeCl2 is linear, BF3 is plana: CH<sub>4</sub> is tetrahedral, NH<sub>3</sub> is pyramidal and water is V-shaped molecule. In order to explain these cases, the valence bond theory has been supplemented by the concept of hybridization. This is a hypothetical concept and has been introduced by Pauling and Slater. According to this concept any number of atomic orbitals of an atom which differ in energy slightly may mix with each other to form new orbitals called hybrid orbitals. The process of mixing or amalgamation of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy is known as hybridization. The following are the rules of hybridization:

- (i) Only orbitals (atomic) of nearly same energy belonging to same atom or ion can take part in hybridization.
- (ii) Number of the hybrid orbitals formed is always equal to number of atomic orbitals which have taken part in the process of hybridization.
- (iii) Most of the hybrid orbitals are similar but they are not necessarily identical in shape. They may differ from one another in orientation in space.
- (iv) Actually the orbitals which undergo hybridization and not the electrons. For example, for orbitals of nitrogen atom  $(2s^2 2p_x^{1}2p_y^{1}2p_z^{1})$  belonging to valency shell when hybridize, form four hybrid orbitals,one of which has two electrons (as before) and other three have one electron each.

No. of atomic orbitals involved in hybridization	Type of hybridization	No. of hybrid orbitals	Shape of molecules		Bond angles	Examples	
. 2	sp (s + p)	2	Linear	**************************************	180°	BeCl <sub>2</sub> , BeF <sub>2</sub>	
3	$sp^2$ $(s+p+p)$	3	Plane triangular		120°	BF <sub>3</sub> , BCl <sub>3</sub>	
4	$sp^3$ $(s+p+p+p)$	4	Tetrahedral		109° 28′	CH <sub>4</sub> , CCl <sub>4</sub>	
4	$dsp^{2}$ one'd' $(d_{x}^{2}-y^{2})$ + one 's' + two 'p'	4	Square planar		90°	[Ni(CN) <sub>4</sub> ] <sup>2-</sup> , [PtCl <sub>4</sub> ] <sup>2-</sup>	
5	$dsp^3$ or $sp^3d$ one 's' + three 'p' + one $d(d_z^2)$	5	Trigonal bipyramid		120° and 90°	PCl <sub>5</sub>	
				*			
6	$d^{2}sp^{3}$ or $sp^{3}d^{2}$ one 's' + three 'p' + two 'd' $(d_{x}^{2}-y^{2},d_{z}^{2})$	6	Octahedral		90°	SF <sub>6</sub>	
7	$d^3sp^3$ or $sp^3d^3$ one 's' + three 'p' + three 'd' ( $d_{xy}$ , $d_{yz}$ , $d_{zx}$ )	. 7 I	Pentagonal bipyramid		72° and 90°	. IF <sub>7</sub>	

(v) The electron waves in hybrid orbitals repel each other and this tend to the farthest apart.

(vi) Hybrid orbitals form only sigma bonds. A hybrid bond is always stronger than a non-hybrid bond. Hybridization increases stability and decreases reactivity and energy of the molecule.

(vii) Depending on the number and nature of orbitals undergoing hybridization, various types of hybrid orbitals directing towards the corners of specified geometrical figures come into existence. The molecule has a **regular geometry** if all the hybrid orbitals after overlapping contain shared pair of electrons, *i.e.*, there are no orbitals containing lone pairs in the valency shell. If, however, the central atom is surrounded by one or more orbitals containing lone pairs of electrons in the valency shell, the geometry of the molecule is **distorted** to some extent. Thus, the presence of one or more orbitals with lone pairs affect the bond angle to some extent due to repulsion between lone pair (pairs) with bonded pair

(pairs). This type of observation has been made, for example, in the molecules of ammonia and water. The following table shows the type of hybridization and the geometry of the molecules containing only bond pairs of electrons.

# Some Typical Cases of Hybridization

(i)  $BeF_2$  molecule: Beryllium atom has the configuration  $1s^2$ ,  $2s^2$ . Since there are no unpaired electrons in the valency shell, it cannot form any covalent bond. Thus, 2s-orbital is first unpaired and an electron is shifted to 2p-orbital.

 Now, there is hybridization between one s- and one p-orbital. Two orbitals (hybrid) of same shape and energy come into existence. These overlap with p-orbital (singly occupied) each of the two fluorine atoms forming two sigma bonds. The molecule formed is linear with a bond angle  $180^{\circ}$ .

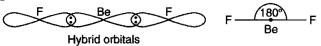


Fig. 2.14 Formation of BeF<sub>2</sub> molecule

(ii) BF<sub>3</sub> molecule: Boron atom has configuration  $1s^2$ ,  $2s^2$   $2p^1$ . In ground state, it has one unpaired orbital which can

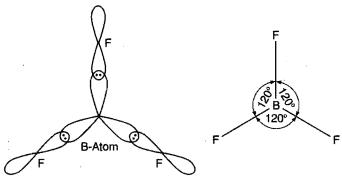


Fig. 2.15 Formation of BF3 molecule

only form only one covalent bond. To get trivalency, the 2s-orbital is unpaired and the electron is shifted to 2p-orbital. Now in excited state the three unpaired orbitals undergo hybridization giving rise to three hybrid orbitals which are 120° apart. The three hybrid orbitals overlap with three p-orbitals from three fluorine atoms forming three sigma bonds. The molecule formed is triangular and planar.

(iii)  $CH_4$  molecule: Carbon atom has configuration  $1s^2$ ,  $2s^2 2p_x^{-1}2p_y^{-1}$ . In ground state, it has two unpaired orbitals which can form only two covalent bonds. To get tetravalency, 2s-orbital is unpaired and the electron is shifted to 2p-orbital. Now in excited state the four unpaired orbitals undergo hybridization giving rise to four hybrid orbitals which are  $109^{\circ}28'$  apart. The four hybrid orbitals overlap with s-orbital of each of the four hydrogen atoms forming four sigma bonds. The molecule formed is tetrahedral.

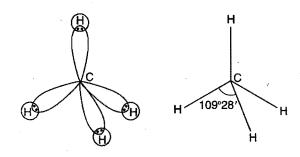


Fig. 2.16 Formation of CH<sub>4</sub> molecule

(iv) PCl<sub>5</sub> molecule: P-atom has configuration  $1s^2$ ,  $2s^22p^6$ ,  $3s^23p_x^1 3p_y^1 3p_z^1$ . In ground state, it can form three covalent bonds as three unpaired orbitals are present in the valency

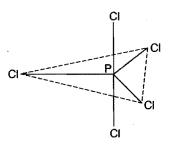
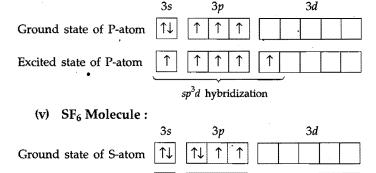


Fig. 2.17 Trigonal bipyramid

shell. To get pentavalency, 3s-orbital is unpaired and the electron is shifted to 3d-orbital. Now, in the excited state the five orbitals involving one s-, one d- and three p-orbitals undergo hybridization giving birth to five hybrid orbitals which overlap with five chlorine atoms forming five sigma bonds. Out of five  $\sigma$ -bonds, three bonds which are located at  $120^{\circ}$  angle are equitorial and the remaining two are axial. Axial bond length is greater.



3s- and paired 3*p*-orbital are unpaired and electrons are shifted to *d*-orbitals. After hybridization six hybrid orbitals directed towards the corners of a regular octahedron come

 $sp^3d^2$  hybridization

Excited state of S-atom

into existence which overlap with six fluorine atoms. The SF<sub>6</sub> molecule has octahedral structure.

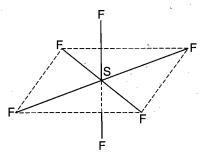


Fig. 2.18

# Geometry of Some Molecules Containing Lone Pairs of Electrons

(i) NH<sub>3</sub> molecu: Nitrogen atom undergoes  $sp^3$  hybridization forming four hybrid orbitals. Three of the hybrid orbitals contain one electron each while the fourth

2s

2p

Ammonia

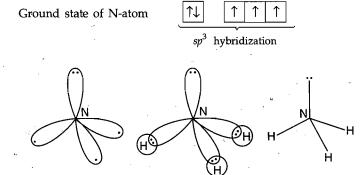


Fig. 2.19

Overlapping with

hydrogen atoms

Hybrid orbitals of N

one has a pair of electrons. Three hybrid orbitals having one electron each overlap with three hydrogen atoms forming three sigma bonds while the lone pair of fourth hybrid orbital remains unused.

The expected bond angle should be 109°28′ but the actual bond angle is 106°45′ because of the repulsion between lone pair and bonded pairs due to which contraction occurs. Thus, ammonia molecule is pyramidal in shape.

(ii) Water molecule: Oxygen atom undergoes  $sp^3$  hybridization forming four hybrid orbitals. Two of the hybrid orbitals contain one electron each while other two a pair of electrons each. The hybrid orbitals having one electron each overlap with hydrogen atoms forming two sigma bonds while the lone pairs of the other hybrid orbitals remain unused.

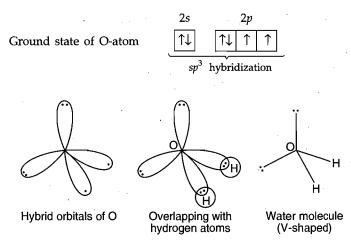


Fig. 2.20

The expected bond angle is 109°28′ but the actual bond angle is 104°35′. This is due to the presence of two lone pairs which repel each other and the bonded pairs more strongly and cause them to come closer and thereby reducing the bond angle from 109°28′ to 104°35′. Similarly, the geometry of PH<sub>3</sub>, PCl<sub>3</sub>, NF<sub>3</sub>, H<sub>2</sub>S, etc., can be explained. It is clear from the above two structures that **higher the number of lone pairs present on a central atom**, **the greater is the contraction caused in the bond angle**. The bond angle is also decreased as the size of the central atom increases. The bond angle in PH<sub>3</sub> is 93°20′.

# Geometry of Molecules Involving Sigma (σ) and Pi (π) Bonds

It is observed that it is not necessary to involve all the orbitals present in the valency shell of the atom in the process of hybridization. The following two examples illustrate this fact;

(i) Ethylene molecule ( $C_2H_4$ ): Ethylene molecule is formed as a result of  $sp^2$  hybridization of carbon. Each carbon atom in excited state undergo  $sp^2$  hybridization giving rise to three hybrid orbitals each. These hybrid orbitals lie in the xy plane while the fourth unhybridized orbital lies at right angle to the hybridized orbitals. In the formation of ethylene two hybrid orbitals, *i.e.*, one from each carbon atom form a sigma bond by head on overlap while the remaining overlap with hydrogen atoms. The unhybridized p-orbitals undergo sidewise overlap to form a  $\pi$ -bond.

Ground state of carbon atom 
$$\uparrow \downarrow$$
  $\uparrow \uparrow \uparrow$ 

Excited state of carbon atom  $\uparrow \downarrow$   $\uparrow \uparrow \uparrow \uparrow$ 
 $p^2$  hybridization

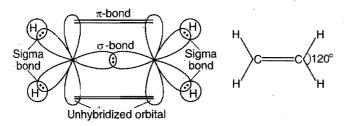


Fig. 2.21 Formation of Ethylene molecule

The molecule of ethylene is planar one:

(ii) Acetylene molecule ( $C_2H_2$ ): Acetylene molecule is formed as a result of sp hybridization of carbon. Each carbon atom in excited state undergoes sp hybridization giving rise to two hybrid orbitals each. Each carbon atom is left with two unhybridized p-orbitals.

Ground state of carbon atom 
$$\uparrow \downarrow \uparrow \uparrow \uparrow \uparrow$$

Excited state of carbon atom  $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$ 
 $p$  hybridization

The two hybrid orbitals of each carbon atom are used up in forming C—C and C—H sigma bonds. The unhybridized orbitals overlap sidewise to form two  $\pi$ -bonds.

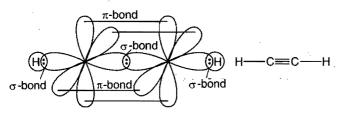


Fig. 2.22 Formation of acetylene molecule

Acetylene has linear structure.

# 2.29 RESONANCE

It is generally observed that a single valence bond structure of a molecule cannot correctly account for the properties of the molecule. In such cases, the concept of resonance is introduced. According to this concept if two or more alternate valence bond structures can be written for a molecule, the actual structure is said to be a resonance or mesomeric hybrid of all these alternate structures. For example, carbon dioxide molecule can be represented by the following three structures:

$$O = C = O \longleftrightarrow \overset{+}{O} = C - \overset{-}{O} \longleftrightarrow \overset{-}{O} - C = \overset{+}{O}$$

The calculated values of bond distances between carbon and oxygen in C=O and C=O are 1.22 Å and 1.10 Å, respectively but the observed bond distance between carbon

and oxygen in carbon dioxide is 1.15 Å. Thus, none of the above structures correctly explains the observed bond length. It is, thus, said that a hybrid form of these structures can provide the exact explanation. The various structures of which the molecule is a resonance hybrid are known as canonical forms or mesomeric forms. Actually resonance hybrid does not oscillate between the canonical forms of a mixture of these forms but it is a definite form and has a definite structure which cannot be written on paper.

# Rules for Selecting Canonical Forms or Mesomeric Forms :

- (i) The relative position of all the atoms in each of the canonical forms must be the same. They should differ only in the position of electrons.
- (ii) The number of unpaired and paired electrons in each of the canonical forms must be same.
- (iii) The contributing structures should not differ much in energy.
- (iv) The contributing structures should be such that negative charge resides on more electronegative and positive charge on the electropositive. Like charges should not reside on atoms close together in the canonical forms.

Formal charges on the atoms in the molecule help us in choosing the most appropriate resonance structure. For example, nitrous oxide molecule is represented by two resonance electron dot structures, one of which has a negative formal charge on the oxygen atom and the other of which has a negative charge on the terminal nitrogen atom.

$$:N \equiv \stackrel{\uparrow}{N} - \stackrel{\circ}{O} : \stackrel{-}{\longleftrightarrow} \stackrel{-}{N} = \stackrel{\uparrow}{N} = \stackrel{\circ}{O}$$

Since oxygen is a more electronegative element than nitrogen, the structure that places a negative formal charge on oxygen is probably lower in energy than the structure that has a negative formal charge on nitrogen.

Thus, the actual structure of  $N_2O$  is  $:N = \stackrel{+}{N} - \stackrel{\bullet}{O}:$ 

(v) As a result of resonance, the bond order changes in many molecules or ions.

Bond order = 
$$\frac{\text{Total number of bonds between two}}{\text{atoms in all the structures}}$$

$$e.g., (a) \longleftrightarrow B.O. = \frac{2+1}{2} = 1.5$$

B.O.=
$$\frac{2+1+1}{3}$$
= 1.33

# Resonance Energy

It has been observed that the molecule which shows resonance has greater heat of formation than the calculated heat of formation of any one of canonical forms. The difference is represented by  $\Delta E$  and its called resonance energy.

$$\Delta E = \begin{pmatrix} \text{Experimental value} \\ \text{of heat of formation} \end{pmatrix} \sim \begin{pmatrix} \text{Calculated value of heat} \\ \text{of formation of most} \\ \text{stable canonical form} \end{pmatrix}$$

On account of  $\Delta E$ , the hybrid form is more stable than any of the canonical forms.

Energy difference between most stable resonating structure and resonance nybrid structure is called resonance energy.

# **■ Some Examples Showing Resonance**

(i) Nitric oxide molecule: It is a resonance hybrid of following two structures:

$$\stackrel{\times}{\times}\stackrel{\times}{N}=0$$
:  $\stackrel{\times}{\longleftarrow}\stackrel{\times}{\times}\stackrel{\times}{N}^{-}=0$ :

(ii) Nitrogen dioxide molecule: It is a resonance hybrid of the following structures:

(iii) Carbonate ion: It is the resonance hybrid of the following forms:

(iv) Ozone:

$$\emptyset$$
  $\longleftrightarrow$   $\emptyset$ 

(v) SO<sub>2</sub> molecule:

(vi)  $NO_3^-$  ion:

$$\begin{bmatrix} 0 \\ 1 \\ N \\ 0 \end{bmatrix} \longleftrightarrow \begin{bmatrix} 0 \\ 1 \\ N \\ 0 \end{bmatrix} \longleftrightarrow \begin{bmatrix} 0 \\ \uparrow \\ N \\ 0 \end{bmatrix}$$

# 2.30 PREDICTION OF GEOMETRY (SHAPE) OF COVALENT MOLECULES

Geometry of a molecule or ion can be predicted if the state of hybridization at central atom is known. The type of hybridization can be known by the following methods:

First Method: The state of hybridization at central atom in a molecule can be known by counting the number of orbitals involved in co-axial overlappings and the number of orbitals with lone pair of electrons, *i.e.*, by counting the number of  $\sigma$ -bonds and the number of lone pair of electrons at central atom. Adding the two, if the total is 4, the hybridization is  $sp^3$ . If this total is 3, the hybridization is  $sp^2$  and if this total is 2, the hybridization is sp.

A few examples are being given below:

#### (a) Beryllium chloride (BeCl<sub>2</sub>)

No. of  $\sigma$ -bonds at Be atom = 2

No. of lone pair of electrons at Be atom = 0

$$Total = 2 + 0 = 2$$

Hybridization is *sp, i.e.*, BeCl<sub>2</sub> is linear and bond angle is 180°.

#### (b) Boron trichloride (BCl<sub>3</sub>)

No. of  $\sigma$ -bonds at B atom = 3

No. of lone pair of electrons at B atom = 0

Total = 3

Hybridization is  $sp^2$ , *i.e.*, BCl<sub>3</sub> is trigonal planar and bond angles are 120° each.

#### (c) Carbon tetrachloride (CCl<sub>4</sub>)

No. of  $\sigma$ -bonds at C atom = 4

No. of lone pair of electrons at C atom = 0

Total = 4

Hybridization is  $sp^3$ , i.e., CCl<sub>4</sub> is tetrahedral and bond angles are  $109^{\circ}28'$  each.

#### (d) Ammonia (NH<sub>3</sub>)

No. of  $\sigma_1$ bonds at N atom = 3

No. of lone pair of electrons at N atom = 1

Total = 3 + 1

= 4

Hybridization is  $sp^3$ .

Shape is trigonal pyramidal (not tetrahedral) and bond angles are not 109°28' but 106°45'.

#### (e) Water (H2O)

No. of  $\sigma$ -bonds at O atom = 2

No. of lone pair of electrons at O atom = 2

Total = 
$$2 + 2 = 4$$

Hybridization is  $sp^3$ .

Shape is angular or V-shape (not tetrahedral) and bond angle is not 109°28′ but 104°35′.

**Second Method:** Number of electron pairs in the valency shell of the central atom can be determined by applying the following formula:

#### For neutral molecules:

No. of electron pairs

= No. of atoms bonded to it  $+\frac{1}{2}$  [Group number

of central atom - Valency of the central atom]

No. of electron pairs at the central atom in CH<sub>4</sub>

$$=4+\frac{1}{2}[4-4]=4$$
 (sp<sup>3</sup> hybridization)

No. of electron pairs at the central atom in PCl<sub>5</sub>

$$= 5 + \frac{1}{2}[5 - 5] = 5$$
 (sp<sup>3</sup>d hybridization)

No. of electron pairs at the central atom in SF<sub>6</sub>

$$= 6 + \frac{1}{2}[6 - 6] = 6$$
 (sp<sup>3</sup>d<sup>2</sup> hybridization)

No. of electron pairs at the central atom in BF<sub>3</sub>

$$= 3 + \frac{1}{2}[3 - 3] = 3$$
 (sp<sup>2</sup> hybridization)

No. of electron pairs at the central atom in H<sub>2</sub>O

$$= 2 + \frac{1}{2}[6 - 2] = 4$$
 (sp<sup>3</sup> hybridization)

#### For ions:

No. of electron pairs = No. of atoms bonded to it

 $+\frac{1}{2}$ [Group number of central atom – Valency of the central atom  $\pm$  No. of electrons]

No. of electron pairs in NH<sub>4</sub><sup>+</sup>

$$=4+\frac{1}{2}[5-4-1]=4$$
 (sp<sup>3</sup> hybridization)

No. of electron pairs in  $SO_4^{2-}$ 

$$=4+\frac{1}{2}[6-8+2]=4$$
 (sp<sup>3</sup> hybridization)

No. of electron pairs in BF<sub>4</sub>

$$=4+\frac{1}{2}[3-4+1]=4$$
 (sp<sup>3</sup> hybridization)

No. of electron pairs	Geometrical figure	Examples	
2	Linear	BeCl <sub>2</sub> , CO <sub>2</sub> , ZnCl <sub>2</sub>	
3	Triangular Planar	BCl <sub>3</sub> , SO <sub>3</sub> , CO <sub>3</sub> <sup>2-</sup>	
4	Tetrahedral	CH <sub>4</sub> , H <sub>2</sub> O, NH <sub>3</sub>	
5	Trigonal bipyramid	PF <sub>5</sub> , ClF <sub>3</sub> , SF <sub>4</sub>	
6	Octahedral	SF <sub>6</sub> , IF <sub>5</sub> , SiF <sub>6</sub> <sup>2-</sup>	

**Third Method:** The number of orbitals involved in hybridization can be determined by the application of the following formula:

$$H = +\frac{1}{2}[V + M - C + A]$$

where H = number of orbitals involved in hybridization

V = valence electrons of central atom

M = number of monovalent atoms linked with central atom

C = charge on the cation

A = charge on the anion

From the value of H, the type of hybridization can be predicted.

Value of H	2	3	4	5	6	7 .	
Hybridization	sp	$sp^2$	$sp^3$	$sp^3d$	$sp^3d^2$	$sp^3d^3$	

### Type 1. Neutral molecules:

(i) 
$$CO_2$$
:  $V = 4$ ,  $M = 0$ ,  $C = 0$ ,  $A = 0$   
 $H = \frac{1}{2} [4 + 0 - 0 + 0] = 2$ ,  $sp$  hybridization

(ii) 
$$SO_2$$
 or  $V = 6$ ,  $M = 0$ ,  $C = 0$ ,  $A = 0$ 

$$SO_3$$
:  $H = \frac{1}{2} [6 + 0 - 0 + 0] = 3$ ,  $sp^2$  hybridization

(iii) 
$$BCl_3$$
:  $V = 3$ ,  $M = 3$ ,  $C = 0$ ,  $A = 0$ 

$$H = \frac{1}{2} [3 + 3 - 0 + 0] = 3$$
,  $sp^2$  hybridization

(iv) 
$$SiCl_4$$
:  $V = 4$ ,  $M = 4$ ,  $C = 0$ ,  $A = 0$ 

$$H = \frac{1}{2} [4 + 4 - 0 + 0] = 4$$
,  $sp^3$  hybridization

(v) 
$$ClF_3$$
:  $V = 7$ ,  $M = 3$ ,  $C = 0$ ,  $A = 0$ 

$$H = \frac{1}{2} [7 + 3 - 0 + 0] = 5, sp^3 d$$
 hybridization

(vi) 
$$XeF_4$$
:  $V = 8$ ,  $M = 4$ ,  $C = 0$ ,  $A = 0$ 

$$H = \frac{1}{2} [8 + 4 - 0 + 0] = 6, sp^3 d^2$$
 hybridization

#### Type 2. When the species is a cation:

(i) 
$$NH_4^+$$
:  $V = 5$ ,  $M = 4$ ,  $C = 1$ ,  $A = 0$   
 $H = \frac{1}{2} [5 + 4 - 1 + 0]$   
 $= 4$ ,  $sp^3$  hybridization

(ii) 
$$CH_3^+$$
:  $V = 4$ ,  $M = 3$ ,  $C = 1$ ,  $A = 0$   
 $H = \frac{1}{2} [4 + 3 - 1 + 0]$   
 $= 3$ ,  $sp^2$  hybridization

(iii) NO<sub>2</sub><sup>+</sup>: V = 5, M = 0, C = 1, A = 0  
H = 
$$\frac{1}{2}$$
 [5 + 0 - 1 + 0]  
= 2, sp hybridization

### Type 3. When the species is an anion:

(i) 
$$CO_3^{2-}$$
:  $V = 4$ ,  $M = 0$ ,  $C = 0$ ,  $A = 2$   
 $H = \frac{1}{2} [4 + 0 - 0 + 2]$   
 $= 3$ ,  $sp^2$  hybridization

(ii) 
$$SO_4^{2-}$$
:  $V = 6$ ,  $M = 0$ ,  $C = 0$ ,  $A = 2$   
 $H = \frac{1}{2}[6 + 0 - 0 + 2] = 4$ ,  $sp^3$  hybridization  
(iii)  $ICl_4^-$ :  $V = 7$ ,  $M = 4$ ,  $C = 0$ ,  $A = 1$   
 $H = \frac{1}{2}[7 + 4 - 0 + 1] = 6$ ,  $sp^3d^2$  hybridization

# 2.31 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Lewis-Langmuir concept of covalent bonding is unable to explain the shapes of the covalent molecules. In case of covalent molecules having three or more atoms, one of the atoms acts as a central atom and rest of the atoms are linked to it in definite directions in space. This definite arrangement of the bonded atoms with the central atom in a molecule is known as shape or geometry of the molecule.

The first simple theory that was put forward to predict the geometry or shape of a covalent molecule is known as Valence Shell Electron Pair Repulsion Theory (or VSEPR theory). This theory was first proposed by Sidgwick and Powell in 1940 and was further developed by Nyholm and Gillespie in 1957.

The theory, known as VSEPR theory, is primarily based on the fact that in a polyatomic molecule, the direction of bond around the central atom depends upon the total number of electron pairs (bonding as well as non-bonding) in its valence shell. These electron pairs place themselves as far apart as possible in space in order to have minimum forces of repulsion between them. The minimum repulsions correspond to the state of minimum energy and maximum stability of the molecule.

The main postulates of VSEPR theory are as follows:

- (i) The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.
- (ii) Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- (iii) The positions of the electron pairs in space around central atom are such that minimise repulsion and thus maximise distance between them.
- (iv) The magnitudes of the different types of electronic repulsions follows the order given below:

These repulsive forces alter the bond angles of the molecule or ion.

(v) The electronic repulsion between two pairs of electrons will be minimum if they are as far apart as possible. On this basis, the following geometrical arrangements are most suited.

No. of 2 3 4 5 6 electron pairs 
Geometrical Linear Triangular Tetra- Trigonal Octafigure 
Examples BeCl<sub>2</sub>, BCl<sub>3</sub>, SO<sub>3</sub> CFl<sub>4</sub>, H<sub>2</sub>O PF<sub>5</sub>, CIF<sub>3</sub>, SF<sub>6</sub>, IF<sub>5</sub> CO<sub>2</sub>, ZnCl<sub>2</sub> 
$$CO_3^{2-}$$
 NH<sub>3</sub> SF<sub>4</sub> SiF $_6^{2-}$ 

(vi) If the central atom is linked to similar atoms and is surrounded by bond pairs of electrons, the repulsions between them are similar. As a result the shape of the molecule is **symmetrical** and the molecule is said to have a **regular geometry**. On the other hand, the molecules in which the repulsive interactions between the electron pairs around the central atom are unequal have **irregular** or **distorted geometry**. In fact, the presence of lone pairs in addition to bond pairs in the molecule causes distortion in the geometry of the molecule. For example, in the NH<sub>3</sub> and H<sub>2</sub>O molecules, the bond angles are not 109°28' but 106.5° and 104.5° respectively due to presence of one lone pair in NH<sub>3</sub> and two lone pairs in H<sub>2</sub>O.

[In the VSEPR notation used to describe molecular geometries, the central atom is denoted as A, terminal atoms as X and lone pairs as E.  $AX_2E_2$  describes a structure with two terminal atoms and two lone pairs around a central atom, for example water molecule. Similarly,  $AX_3E_2$  describes a structure with three terminal atoms and two lone pairs around a central atom. For example CIF<sub>3</sub> molecule.]

(vii) A multiple bond is treated as if it is a single electron pair and two or three electron pairs of a multiple bond are treated as a single super pair.

(viii) Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

## A Strategy for Applying VSEPR Method

To predict the shape of a molecule or polyatomic ion, the following four steps can be followed:

**Step 1:** Draw a Lewis structure of the molecule or polyatomic ion. The structure must be plausible but it does not need to be the best one.

**Step 2:** Determine the number of electron groups around the central atom (bonding and non-bonding both). A double and a triple bond each is counted as one electron group.

**Step 3:** Identify the electron group geometry. This may be linear, trigonal planar, tetrahedral, trigonal bipyramidal or octahedral corresponding to two, three, four, five and six electron groups respectively.

**Step 4:** Identify the molecular geometry. This is based on the positions around the central atom occupied by other atoms (not by lone pairs).

Molecular Geometry Around Atoms with 2, 3, 4, 5 and 6 charge clouds (Total number electron pairs-bonding and non-bonding)

Number of Bonds (a)	Number of Lone Pairs (b)	Total Number of Charge Clouds (a + b)	notation	Molecular Geometry	Example
2	0	2	AX <sub>2</sub>	O-O Linear	Cl—Be—Cl
[3	0	. 3	$AX_3$	Trigonal planar	F <sub>F</sub> B-F
2	1	. 3	AX <sub>2</sub> E	planar Bent	o>s-:
4	0		AX <sub>4</sub>	Tetrahedral	H - C-H
3	1	. 4	$AX_3E$	O Trigonal	H H
2	2		$AX_2E_2$	O Bent	H-0-:
5	0		AX <sub>5</sub>	Trigonal bipyramidal	CI CI CI CI
4	1	5	$AX_4E$	Sec-saw	F   S   -:
3	2		$AX_3E_2$	T-shaped	F Cl-F F
2	3		$AX_2E_3$	Linear	
6	0		$AX_6$	Octahedral	F F F F
5	1	6 .	$AX_6$ $AX_5E$ $AX_4E_2$	Square pyramidal	$\begin{bmatrix} F \\ F \\ S \\ F \end{bmatrix} = \begin{bmatrix} F \\ F \\ F \end{bmatrix}$ $\begin{bmatrix} CI \\ CI \\ SI \\ CI \end{bmatrix}^{2}$
	2		AX <sub>4</sub> E <sub>2</sub>	O. O. O. O. O. O. O. O. O. O. O. O. O. O	

### illustration of the Theory by Considering a Few Examples

#### (A) Molecules containing bond pairs only

(i) Shape of BeF<sub>2</sub> molecule: Be-atom is surrounded by two bond pairs of electrons. These should be localised in such a way that there is minimum repulsion between them, *i.e.*, bond angle should be 180°, hence BeF<sub>2</sub> molecule is **Linear**.

Molecules such as BeCl<sub>2</sub>, ZnCl<sub>2</sub>, HgCl<sub>2</sub>, etc., have a linear shape.

(ii) Shape of  $BF_3$  molecule: The Lewis structure of  $BF_3$  is:

$$F \overset{\bullet}{\underset{\bullet}{\times}} B \overset{\bullet}{\underset{\bullet}{\times}} F$$

B-atom is surrounded by three bond pairs. According to VSEPR theory they must be situated at an angle of 120° as they will experience minimum repulsion, *i.e.*, shape of BF<sub>3</sub> is **triangular planar**.

Molecules such as BCl<sub>3</sub>, AlCl<sub>3</sub>, etc., have a triangular planar shape.

(iii) Shape of  $CH_4$  molecule: The Lewis structure of  $CH_4$  is:

C-atom is surrounded by four bond pairs. These four bond pairs adopt tetrahedral structure as to remain as far apart as possible in order to have minimum repulsion. The bond angle is  $109^{\circ}28'$  (or approximately  $109.5^{\circ}$ ). Species such as  $SiF_4$ ,  $CCl_4$ ,  $SiH_4$ ,  $NH_4^{\dagger}$ , etc., have tetrahedral structure.

(iv) Shape of PCl<sub>5</sub> molecule: The Lewis structure of PCl<sub>5</sub> is:

P-atom is surrounded by five bond pairs. To have minimum energy, the bond pairs of electrons should be as far apart as possible from each other. This is possible if the molecule acquires a **trigonal bipyramidal** shape. In this geometry all the bond angles are not equal. The axial bonds are of 90° and the bond angles in the triangle plane are of 120°. Two axial P—Cl bonds are longer as compared to three equatorial bonds. This is due to the fact that axial bond experiences greater repulsion from other bonds.

Molecules such as PF<sub>5</sub>, SbCl<sub>5</sub>, etc., have same shape.

(v) Shape of  $SF_6$  molecule: The Lewis structure of  $SF_6$  is:



S-atom is surrounded by six bond pairs. According to VSEPR theory these bond pairs adopt an **octahedral** geometry. In this geometry, all the bond angles are  $90^{\circ}$  each. The molecule is symmetrical and stable, *i.e.*, less reactive. TeF<sub>6</sub> molecule is also expected to have the same shape.

#### (B) Molecules containing lone pairs and bond pairs

(1) Molecules containing two bonding electron pairs and one lone pair  $(AX_2E)$ : The molecule contains three electron pairs. Thus, it should have a trigonal planar geometry. Due to the presence of one lone pair, the geometry gets distorted. For example,  $SO_2$  has a V-shaped geometry. The bond angle is reduced to 119.5°.

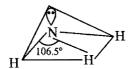


Shape of SO<sub>2</sub> molecule

- (2) Molecule containing four electron pairs
- (a) Molecules containing three bonding electron pairs and one lone pair  $(AX_3E)$

Shape of  $NH_3$  molecule: The Lewis structure of  $NH_3$  is:

N-atom is surrounded by four electron pairs (three bonded and one lone pair). These four pairs adopt tetrahedral geometry. Due to presence of lone pair, NH<sub>3</sub> has a distorted tetrahedral geometry. The bond angle is not 109°28' but it is 106.5°. The actual shape of ammonia molecule is **pyramidal**.



Shape of NH<sub>3</sub> molecule

Molecules such as  $PCl_3$ ,  $NF_3$ ,  $H_3O^+$ , etc., have same shape. (b) Molecules containing two bonding electron pairs and two lone pairs  $(AX_2E_2)$ 

**Shape of water molecule:** The Lewis structure of water is:

O-atom is surrounded by four electron pairs (two bonded and two lone pairs). These four electron pairs adopt

tetrahedral arrangement. The presence of two lone pairs brings distortion in the geometry of the molecule. The lone pairs repel the bond pairs more effectively resulting in the decrease of bond angle from 109°28' to 104.5°. The actual shape of the water molecule is V-shape.

Molecules/ions such as  $F_2O$ ,  $NH_2^-$ ,  $SCl_2$ ,  $PbCl_2$ , etc., have shape similar to water molecule.



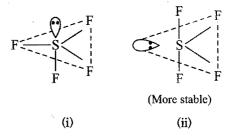
Shape of H<sub>2</sub>O molecule

(3) Molecules containing five electron pairs

(a) Molecules containing four bonding electron pairs and one lone pair  $(AX_4E)$ 

The example is  $SF_4$  molecule. The molecule has five electron pairs and should have trigonal bipyramidal geometry in which one position is occupied by a lone pair.

Therefore, SF<sub>4</sub> molecule can have either of the following two structures.



In structure (i) the lone pair is on axial position while in structure (ii) the lone pair is on equatorial position. The structure (ii) will therefore, experience lesser repulsions than structure (i). Thus the structure (ii) which is described as distorted tetrahedron or a folded square or see-saw will be a more stable correct structure of SF<sub>4</sub>. The bond angles are 89° and 117° instead of 90° and 120° respectively.

## -(b) Molecules containing three bonding electron pairs and two lone pairs $(AX_3E_2)$

The example is ClF<sub>3</sub>. The molecule has five electron pairs and it should have a trigonal bipyramidal geometry in which two positions are occupied by lone pairs. Therefore, the molecule, ClF<sub>3</sub>, can have either of the following three structures.

Structure (i) is most stable as it will experience lesser repulsions in comparison to structures (ii) and (iii). Thus, the molecule has a T-shaped structure and bond angle is 87.6°.

# (c) Molecules containing two bonding electron pairs and three lone pairs $(AX_2E_3)$

The example is XeF<sub>2</sub>. It has five electron pairs and it should have a trigonal bipyramidal geometry in which three positions are occupied by lone pairs. If the three lone pairs are present on the corners of an equatorial triangle, the net repulsion will be zero.

Thus, the most correct and stable shape will be linear.



Linear shape

#### (4) Molecules containing six electron pairs

# (a) Molecules containing five bonding electron pairs and one lone pair $(AX_5E)$

The example is BrF<sub>5</sub>. It has six electron pairs and it should have an octahedral geometry in which one position is occupied by a lone pair. Since all the six positions in octahedron are equivalent, the lone pair can be present on any one position. Thus, the molecule has a square pyramidal geometry.



# (b) Molecules containing four bonding electron pairs and two lone pairs $(AX_4E_2)$

The example is XeF<sub>4</sub>. It has six electron pairs and should have octahedral geometry in which two positions are occupied by lone pairs.



The shape of the molecule is square planar.

## 2.32 BOND CHARACTERISTICS

Covalent bonds are characterised by the following four parameters:

- (1) Bond length
- (2) Bond energy
- (3) Bond angle
- (4) Bond order

#### (1) Bond Length:

The distance between the nuclei of two atoms bonded together is termed bond length or bond distance. It is expressed in angstrom (Å) or picometre (pm) units:

$$[1 \text{ Å} = 10^{-8} \text{ cm}; 1 \text{ pm} = 10^{-12} \text{ m}]$$

#### **BOND LENGTHS**

Bond	Bond length (Å)	Bond	Bond length (Å)
НН	0.74	H—F	0.92
(in H <sub>2</sub> )	-	(in HF)	·
Cl—Cl	1.99	H—Cl	1.27
(in Cl <sub>2</sub> )		(in HCl)	
Br-Br	2.28	HBr	1.41
(in Br <sub>2</sub> )		(in HBr)	
II	2.67	H—I	1.61
$(in, I_2)$		(in HI)	
F—F	1.42	ОН	0.96
(in FA		(in H <sub>2</sub> O)	
C—C	1.54	0=0	1.21
		(in O <sub>2</sub> )	,
C=C	1.34	C-O	1.43
(in $C_2H_4$ )		(in alcohols)	
C≡C	1.21	C=O	1.22
(in $C_2H_2$ )		(in aldehydes)	
C-N	1.47	N—H	1.03
(in amines)			
C—H	1.08	S—H	1.35
(in organic		NO	1.36
molecules)		N=0	1.22

Bond lengths are measured spectroscopically or by X-ray diffraction of solids and electron diffraction of gases. In ionic compounds, bond length is obtained by adding up of the ionic radii of two bonded ions.

Bond length in ionic compound =  $r_c^+ + r_a^-$ 

Similarly, in a covalent compound, bond length is obtained by adding up the covalent (atomic) radii of two bonded atoms.

Bond length in covalent compound  $(AB) = r_A + r_B$ 

The factors such as resonance, electronegativity, hybridization, steric effects, etc., which affect the radii of atoms, also apply to bond lengths, *i.e.*, the values of bond lengths do not hold good for all the compounds. Bond lengths of some common bonds are tabulated in the table given above.

When there is large difference in electronegativity of the two atoms, the bond length is generally less than the sum of the covalent radii of the two atoms.

#### Important features:

(i) The bond length of the homonuclear diatomic molecules are twice the covalent radii. Bond length increases with the increase in the size of atoms.

(ii) The lengths of double bonds are less than the lengths of single bonds between the same two atoms and triple bonds are even shorter than double bonds.

Single bond > Double bond > Triple bond

(iii) Bond length decreases with increase in s-character since s-orbital is smaller than a p-orbital.

$$sp^3$$
 C—H = 1.112 Å;  $sp^2$  C—H = 1.103 Å; (25% s-character as in alkanes) as in alkenes)  $sp$  C—H = 1.08 Å (50% s-character as in alkynes)

- (iv) Bond length of polar bond is smaller than the theoretical non-polar bond length.
- (v) Bond length is affected by resonance and hyperconjugation.

#### (2) Bond Energy or Bond Strength:

Bond energy or bond strength is defined as the amount of energy required to break a bond in a molecule. Each bond has a characteristic value of this energy and is measure of the strength of the bond. It is generally observed that shorter the bond length, greater is the bond strength or bond energy of the bond.

$$H \rightarrow H(g) \longrightarrow 2H(g)$$
  $\Delta H = 436 \text{ kJ mol}^{-1}$  (Bond length = 0.74 Å)  
 $Cl \rightarrow 2Cl(g)$   $\Delta H = 242 \text{ kJ mol}^{-1}$  (Bond length = 1.99 Å)  
 $H \rightarrow Cl(g) \longrightarrow H(g) + Cl(g)$   $\Delta H = 431 \text{ kJ mol}^{-1}$  (Bond length = 1.27 Å)

Consider the dissociation of water molecule which consists of two O—H bonds.

$$H-O-H(g) \longrightarrow 2H(g) + O(g);$$
  $\Delta H = 926 \text{ kJ mol}^{-1}$ 

The average bond energy of O—H bond =  $\frac{926}{2}$  = 463 kJ

Similarly, the average bond energy of C—H bond in  $CH_4$  is equal to one-fourth of the energy of dissociation of  $CH_4$  into (C+4H). However, the bond energy of each C—H bond in  $CH_4$  is different.

$$CH_4(g) \longrightarrow CH_3(g) + H(g);$$
  $\Delta H = 426 \text{ kJ mol}^{-1}$   
 $CH_3(g) \longrightarrow CH_2(g) + H(g);$   $\Delta H = 439 \text{ kJ mol}^{-1}$   
 $CH_2(g) \longrightarrow CH(g) + H(g);$   $\Delta H = 451 \text{ kJ mol}^{-1}$   
 $CH(g) \longrightarrow C(g) + H(g);$   $\Delta H = 347 \text{ kJ mol}^{-1}$   
 $CH_4(g) \longrightarrow C(g) + 4H;$   $\Delta H = 1663 \text{ kJ mol}^{-1}$ 

Hence, average bond energy C—H =  $\frac{1663}{4}$  = 416 kJ mol<sup>-1</sup>

Thus, the bond energy of C—H bond depends on the order in which the particular hydrogen atom is lost from the molecule. A similar situation exists for all molecules with more than two atoms. The strengths of the bonds depend on the order in which they are broken. Average bond energies of some common bonds are listed below:

BOND ENERGIES IN kJ mol<sup>-1</sup>

	. *		
Bond	Bond energy	Bond	Bond energy
Н—Н	436	Cl—Cl	242
O=O	497	Br—Br	193
N≡N	945	I—I ·	151
F—F	158	$H$ $\longrightarrow$ $F$	563
H—Cl	431	N—H	389
:		(in NH <sub>3</sub> )	·.
H—Br	366	О—Н	464
		(in water)	
H—I	299	C—C	346
C—H	416	C = C	598
(in methane)		(in C <sub>2</sub> H <sub>4</sub> )	

#### Important features:

- (i) The magnitude of the bond energy depends on the type of bonding. Most of the covalent bonds have energy between 50 to 100 kcal  $\text{mol}^{-1}$  (200–400 kJ  $\text{mol}^{-1}$ ). Strength of sigma bond is more than that of a  $\pi$ -bond.
- (ii) A double bond in a diatomic molecules has a higher bond energy than a single bond and a triple bond has a higher bond energy than a double bond between the same atoms.

$$C \equiv C > C = C > C - C$$

- (iii) The magnitude of the bond energy depends on the size of the atoms forming the bond, *i.e.*, bond length. Shorter the bond length, higher is the bond energy.
- (iv) Resonance in the molecule affects the bond energy.
- (v) The bond energy decreases with increase in number of lone pairs on the bonded atom. This is due to electrostatic repulsion of lone pairs of electrons on the two bonded atoms.
- (vi) Homolytic and heterolytic fission involve different amounts of energies. Generally the values are low for homolytic fission of the bond in comparison to heterolytic fission.
- (vii) Bond energy decreases down the group in case of similar molecules.
- (viii) Bond energy increases in the following order:

$$s 
C—C > N—N > O—O
346 163 146.4 kJ mol<sup>-1</sup>
(No lone pair) (One lone pair) (Two lone pairs)$$

(ix) Bond energy of covalent molecule can be calculated using Pauling's formula.

$$E_{A-B} = 1/2 [E_{A-A} + E_{B-B}] + 23 (x_A - x_B)^2$$
 where  $E_{A-B}$ ,  $E_{A-A}$  and  $E_{B-B}$  are the bond energies of the molecules  $A-B$ ,  $A_2$  and  $B_2$  respectively and  $xA$  and  $xB$  are the electronegativity of  $A$  and  $B$ .  $A$  more accurate

value is obtained when geometric mean  $\sqrt{E_{A-A}\times E_{B-B}}$  is used instead of arithmetic mean,  $\frac{E_{A-A}+E_{B-B}}{2}$ .

## ■ (3) Bond Angles

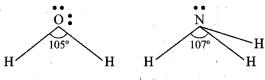
Angle between two adjacent bonds at an atom in a molecule made up of three or more atoms is known as the bond angle. Bond angles mainly depend on the following three factors:

(i) **Hybridization**: Bond angle depends on the state of hybridization of the central atom.

Hybridization	$sp^3$	$sp^2$	sp
Bond angle	109°28′	120°	180°
Example	$CH_4$	$BCl_3$	BeCl <sub>2</sub>

It is observed that as s-character increases in the hybrid bond, the bond angle increases.

(ii) Lone pair repulsion: Bond angle is affected by the presence of lone pair of electrons at the central atom. A lone pair of electrons at the central atom always tries to repel the shared pair (bonded pair) of electrons. Due to this, the bonds are displaced slightly inside resulting in a decrease of bond angle. The bond angle in NH<sub>3</sub> is  $107^{\circ}$  and bond angle in H<sub>2</sub>O is  $105^{\circ}$  inspite of the fact that N-atom and O-atom undergo  $sp^3$  hybridization.



Water molecule

Ammonia molecule

(iii) **Electronegativity**: If the electronegativity of the central atom decreases, bond angle decreases.

In case the central atom remains the same, bond angle increases with decrease in the electronegativity of the surrounding atoms.

#### (4) Bond order

Bond order is defined as the number of bonds or number of shared electron pairs between two atoms in a molecule.

Н—Н	or	H : H	Bond order = $1$
O=O	or	0::0	Bond order $= 2$
N≡N	or	N : N	Bond order $= 3$
C≡O	or	C : O	Bond order $= 3$

Isoelectronic molecules or ions have same bond order.

For example,  $F_2$  and  $O_2^{2-}$  (18 electrons) have bond order 1.  $N_2$ , CO and  $NO^+$  (14 electrons) have bond order 3.

It is observed that with increase in bond order, bond enthalpy increases while bond length decreases.

## 2.33 ODD ELECTRON BONDS

In 1916 Luder postulated that there are number of stable molecules in which double bonds are formed by sharing of an odd number of electrons, i.e., one, three, five, etc., between

the two bonded atoms. The bonds of this type are called odd electron bonds.

An example of one electron bond is found in the hydrogen molecule ion,  $H_2^+$ . It has a bond energy of 61 kcal/mol. The ion is less stable than  $H_2$  molecule as a bond length is longer than two electrons bond in  $H_2$ . The excited state of alkali metal molecules involve odd electron bonds. Thus,  $\text{Li}_2^+$ ,  $\text{K}_2^+$ ,  $\text{Na}_2^+$  are all bound by one electron.

 $\text{He}_2^+$  ion,  $\text{O}_2$  molecule, nitric oxide molecule, nitrogen dioxide molecule, etc., are the examples of three electrons bonds.  $\text{He}_2^+$ ion is a resonance hybrid of following two forms:

$$He_{\times}^{\times} \cdot He^{+} \longleftrightarrow He^{+} \cdot_{\times}^{\times} He$$

The normal valence bond structure of oxygen molecule,  $\overset{\star\star}{\cdot \circ} = \overset{\star\times}{O_{\times}}^{\times}$ , fails to account for the paramagnetic nature of oxygen. Thus, structure involving three electrons bond has been suggested by Pauling. The following structure:

explains the paramagnetic nature and high dissociation energy of oxygen molecule.

#### **№** Properties of Odd Electron Bonds

- (i) The odd electron bonds are generally established either between two like atoms or between different atoms which have not more than 0.5 difference in their electronegativities.
- (ii) Odd electron bonds are approximately half as strong as a normal covalent bond.
- (iii) Molecules containing odd electrons are extremely reactive and have the tendency to dimerise.
- (iv) Bond length of one electron bond is greater than that of a normal covalent bond. Whereas the bond length of a three electron bond is intermediate between those of a double and a triple bond.
- (v) One electron bond is a resonance hybrid of the following two structures:

$$A \bullet B \longleftrightarrow A \bullet B$$

Similarly, a three electron bond is a resonance hybrid of the following two structures:

$$A \bullet B \longleftrightarrow A \bullet B$$

## 2.34 MOLECULAR ORBITAL THEORY

The valence bond theory is based on the assumption that the formation of a molecule involves an interaction between the electron waves of only those atomic orbitals of the participating atoms which are half filled. These atomic orbitals mix with one another to form a new orbital of greater stability while all other orbitals on the atoms remain undisturbed or maintain their individual identity. But this cannot be correct because the nucleus of one approaching atom is bound to affect the electron waves of nearly all the orbitals of the other atom. Besides this, the valence bond theory fails to explain the formation of coordinate bond, the

paramagnetic character of  $O_2$  molecule and the formation of odd electron molecules or ions such as  $H_2^+$  ion where no pairing of electron occurs.

Molecular orbital theory of chemical bonding is more rational and more useful in comparison to valence bond theory. This theory was put forward by Hund and Mullikan. According to this theory, all the atomic orbitals of the atoms participating in molecule formation get disturbed when the concerned nuclei approach nearer. They all get mixed up to give rise to an equivalent number of new orbitals that belong to the molecule now. These are called molecular orbitals. The electrons belonging originally to the participating atoms are now considered to be moving along the molecular orbitals under the influence of all the nuclei. Thus, molecular orbitals are polycentric. Molecular orbital is defined as the region in space comprising the nuclei of the combining atoms around which there is maximum probability of finding the electron density.

Molecular orbitals are of varying energies and are arranged in the order of increasing energy levels as in the case of atomic orbitals. The filling of electrons in the molecular orbitals follows, aufbau principle and Hund's rule.

## Linear Combination of Atomic Orbitals (LCAO)

Molecular orbitals of a molecule are obtained by the linear combination of atomic orbitals of the bonded atoms. The electron waves that describe the atomic orbitals have positive and negative phase or amplitude just as there are positive (upward) and negative (downward) amplitudes associated with standing wave. When waves are combined, they may interact either constructively or destructively. If the two identical waves are added, they combine constructively to produce the wave with double the amplitude and same wavelength. Conversely, if they are subtracted, they combine destructively to produce the wave with zero amplitude. This has been shown in Fig. 2.23.

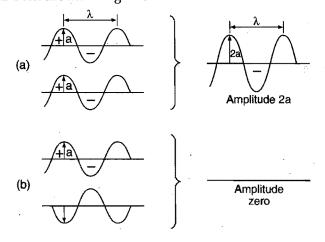


Fig. 2.23

Likewise when two atomic orbitals overlap they can be in phase (added) or out of phase (subtracted). If they overlap in phase, constructive interaction occurs in the region between two nuclei and a **bonding orbital** is produced. When they overlap out of phase, destructive interference reduces the probability of finding an electron in the region between the nuclei and **antibonding orbital** is produced.

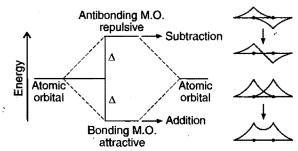


Fig. 2.24 Formation of bonding and antibonding molecular orbitals

This can be shown mathematically also. Suppose  $\psi_A$  and  $\psi_B$  represent the amplitude (or also called wave functions) of the electron waves of the atomic orbitals of the two atoms A and B respectively. When these waves overlap, two cases may arise:

Case I. When the two waves are in phase, *i.e.*, constructive interference occurs, the waves are added so that the amplitude of the new wave is

$$\phi = \psi_A + \psi_B$$

Case II. When the two waves are out of phase, *i.e.*, destructive interference occurs, the waves are subtracted from each other so that the amplitude of the new wave is

$$\phi' = \psi_A - \psi_B$$

The probable electron density is given by the square of the amplitude, therefore we have

$$\phi^{2} = (\psi_{A} + \psi_{B})^{2} = \psi_{A}^{2} + \psi_{B}^{2} + 2\psi_{A}\psi_{B}$$
and
$$\phi'^{2} = (\psi_{A} - \psi_{B})^{2} = \psi_{A}^{2} + \psi_{B}^{2} - 2\psi_{A}\psi_{B}$$
i.e.,
$$\phi^{2} > \psi_{A}^{2} + \psi_{B}^{2}$$
whereas  $\phi'^{2} < \psi_{A}^{2} + \psi_{B}^{2}$ 

The above relation shows that the probability of finding the electrons in the bonding molecular orbital increases whereas it decreases in the antibonding molecular orbital. In other words, it can be said that electron density is high between the nuclei of two bonded atoms due to increased attraction in case of bonding molecular orbital whereas most of the electron density is located away from the space between the nuclei due to repulsion in case of antibonding molecular orbital. In fact, there is a nodal plane between the two nuclei of antibonding molecular orbital where electron density is zero.

Just as letters s, p, d, etc., are used to denote the atomic orbitals, similarly Greek symbols,  $\sigma$ ,  $\pi$ ,  $\delta$ , etc., are used to denote the bonding molecular orbitals and asterisk symbols

 $\sigma^*$ ,  $\pi^*$ ,  $\delta^*$ , etc., are used to represent antibonding molecular orbitals.

Note: Crests of the electron waves are given '+' sign and troughs a '-' sign. Thus, bonding molecular orbital is formed by combination of '+' with '+' and '-' with '-' part of the electron waves whereas antibonding molecular orbital is formed by combination of '+' with '-' part of the electron waves.

The energy of the bonding molecular orbital is always lower than the energy of the atomic orbitals of the combining atoms whereas the energy of the antibonding molecular orbital is higher than the energy of the combining atomic orbitals as bonding molecular orbital is more stable and antibonding molecular orbital is less stable. However, it should be noted that compared with the energy of the combining atomic orbitals, the energy of the antibonding molecular orbital is raised by an amount greater than the amount by which the energy of the bonding orbital is lowered but the sum of the energies of bonding molecular orbital and antibonding molecular orbital is equal to the sum of energies of the combining atomic orbitals. The lowering in energy ( $\Delta$ ) of the bonding molecular orbital than the combining atomic orbital is called stabilization energy while increase in energy ( $\Delta'$ ) of the antibonding molecular orbital is called destabilizing energy.

#### Distinction between Atomic and Molecular Orbitals

	Atomic orbital	Molecular orbital
1.	<i>i.e.</i> , electron cloud extends around the nucleus of a single	Molecular orbital is polycentric, i.e., the electron cloud extends around all the nuclei of bonded atoms in
•	atom.	the molecule.
2.	It is less stable.	It is more stable.
3.	It has simple shape.	It has complex shape.
4.	Atomic orbitals are designated	Molecular orbitals are designated
	as <i>s</i> , <i>p</i> , <i>d</i> , etc.	as σ, σ*, π, π*, etc.

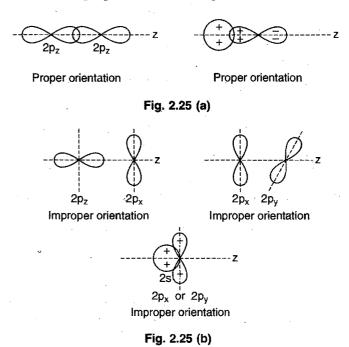
## Comparison of Bonding and Antibonding Molecular Orbitals

Bonding molecular orbitals	Antibonding molecular orbitals
combination of two atomic	It is formed by linear combination of two atomic orbitals when their wave functions are subtracted.
2. Its energy is less than the combining atomic orbitals.	Its energy is more than the combining atomic orbitals.
3. It increases the electron density between the nuclei. It therefore stabilises the molecule.	It decreases the electron density between the nuclei. It therefore destabilises the molecule.
4. It has no nodal plane (plane where electron density is zero).	It has nodal plane. It is symmetrical about inter-
5. It is symmetrical about internuclear axis.	nuclear axis and about a line perpendicular to it.
6. Designated by $\sigma$ , $\pi$ , $\delta$ , etc.	Designated by σ, π, δ, etc.

## Conditions for Combination of Atomic Orbitals to form Molecular Orbitals

The formation of molecular orbitals by linear combination of atomic orbitals can take place only if the following conditions are fulfilled:

- (i) The combining atomic orbitals must have same or nearly same energy, *i.e.*, comparable energy. For homonuclear diatomic molecule,  $A_2$ , 1s atomic orbital of one atom can combine with 1s atomic orbital of another atom or 2s can combine with 2s, 2p with 2p and so on. 1s cannot combine with 2s or 2s cannot combine with 2p as the energy difference is appreciably high. However, such combination can take place for heteronuclear diatomic molecules, AB, if the energy difference is not very high.
- (ii) The combining atomic orbitals must have proper orientation, *i.e.*, same symmetry about the molecular axis. For example, taking z-axis as the molecular axis,  $2p_z$  orbital of one atom can overlap with  $2p_z$  orbital of another atom but not with  $2p_x$  or  $2p_y$  orbitals because of their different symmetries. Similarly 2s orbital of one atom can overlap with  $2p_z$  orbital but not with  $2p_x$  or  $2p_y$  orbital of another atom on account of improper orientation (Fig. 2.25 a and 2.25 b).



(iii) The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlap, the greater will be the electron density between the nuclei of a molecular orbital.

#### Salient Features of Molecular Orbital Theory

From the above discussion, the main features of the molecular orbital theory can be summed up as follows:

- (i) Like valence bond theory, this theory starts with atomic orbitals but the atomic orbitals of the atoms approaching for bonding overlap to undergo constructive interference as well as destructive interference to form molecular orbitals. As a result, the atomic orbitals lose their individual identity and all the electrons in the molecule are associated with molecular orbitals.
- (ii) When two atomic orbitals overlap, they form two new orbitals called molecular orbitals. One of which is called bonding molecular orbital and other is called antibonding molecular orbital. These are formed by addition and subtraction of wave functions respectively.
- (iii) Molecular orbitals are the energy states of a molecule in which the electrons of the molecule are filled.
- (iv) Bonding molecular orbital has energy lower than the combining atomic orbitals while antibonding orbital has higher energy than the combining atomic orbitals.
- (v) Only those atomic orbitals can overlap to form molecular orbitals which have comparable energies and proper orientation.
- (vi) Electrons present in the bonding molecular orbital contribute towards the stability of molecule while electrons present in antibonding molecular orbital contribute to the repulsions between the nuclei of the atoms.
- (vii) The bonding molecular orbitals are denoted as  $\sigma$ ,  $\pi$ ,  $\delta$ , etc., while antibonding molecular orbitals are denoted as  $\sigma^*$ ,  $\pi^*$ ,  $\delta^*$ , etc.
- (viii) A molecular orbital (bonding or antibonding cannot accommodate more than two electrons. Both the electrons must have opposite spins (Pauli's exclusion principle).
- (ix) Molecular orbitals are filled in order of increasing energies starting with the orbital of minimum energy (aufbau principle).
- (x) In molecular orbitals of same energy (degenerate orbitals), the electron pairing occurs only when all of them are singly filled (Hund's rule).
- (xi) The shapes of the molecular orbitals formed depend upon the type of the combining orbitals.

### Types of Molecular Orbitals Formed

When the two atomic orbitals overlap along the internuclear axis, the molecular orbitals formed are called  $\sigma$  and  $\sigma^*$  molecular orbitals and when overlap sideways, the molecular orbitals formed are called  $\pi$  and  $\pi^*$  molecular orbitals. As s-orbitals are spherical symmetrical, their wave function has same sign in all directions while in case of p-orbitals, one lobe is given '+' sign and other a '-' sign. Overlapping of '+' lobes or '-' lobes of two p-orbitals forms bonding molecular orbital and overlapping of one '+' lobe of one orbital and '-' lobe of other orbital forms antibonding

molecular orbital. '+' lobe interaction with '+' lobe means addition of wave functions while '+' lobe interaction with '-' lobe means subtraction of wave functions. Few simple cases of combination of atomic orbitals are discussed:

(i) Molecular orbitals from s-atomic orbitals: The formation of molecular orbitals by linear combination of 1s atomic orbitals of two atoms is shown in Fig. 2.26.

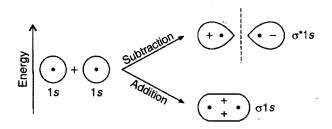


Fig. 2.26

The wave functions of two 1s atomic orbitals can combine in two ways:

- (a) When both have same sign, *i.e.*, addition of wave functions occur and  $\sigma$  1s molecular orbital is formed. This overlap takes place along the internuclear axis.
- (b) When both have opposite sign, *i.e.*, subtraction of wave functions occur and  $\sigma^*$  1s molecular orbital (antibonding) is formed. This overlap takes place also along the internuclear axis. The dotted line between the two lobes indicates a nodal plane where the probability of finding the electron density is zero.

Each of the two molecular orbitals can accommodate two electrons each and four in all. Similarly, the combination of two 2s-orbitals forms two molecular orbitals  $\sigma$ 2s (bonding)  $\overset{*}{\sigma}$ 2s (antibonding).

- (ii) Molecular orbitals from *p*-atomic orbitals: The two 2*p*-orbitals can combine together in either of the two ways, *i.e.*, end-to-end or side-by-side.
- (a) End-to-end overlap: Let z-axis be the line joining the two nuclei in the molecule. Thus, only  $2p_z$  orbitals will combine in end-to-end fashion. When  $2p_z$  orbitals on two atoms combine in phase (addition), bonding molecular orbital designated as  $\sigma 2p_z$  and when these overlap out of phase (subtraction), antibonding molecular orbital  $\sigma 2p_z$  come into existence. The formation is shown in Fig. 2.27.
- (b) Side-by-side overlap: When two  $2p_y$  orbitals or  $2p_x$  orbitals on two atoms, which have mutually parallel axis, interact to give rise molecular orbitals that are not symmetrical about nuclear axis and are called  $\pi$ -molecular orbitals. These are designated as  $\pi 2p_y$  (bonding) and  $\pi 2p_y$  (antibonding). Similarly, when two  $2p_x$  orbitals on the two atoms interact they form two  $\pi$ -molecular orbitals which are designated as  $\pi 2p_x$  (bonding) and  $\pi 2p_x$  (antibonding). The formation has been shown in Fig. 2.27.

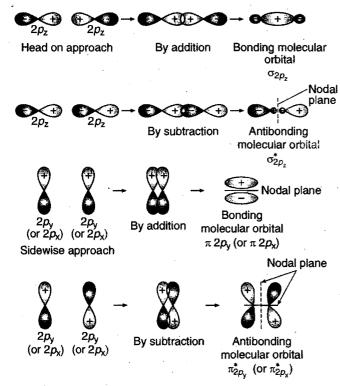


Fig. 2.27 Combination of two 2p atomic orbitals

Thus, in all there are six molecular orbitals arising from two sets of 2p atomic orbitals. Since,  $2p_y$  and  $2p_x$  atomic orbitals on an atom are degenerate (equal energy), the  $\pi$  molecular orbitals formed by these orbitals will also be degenerate, *i.e.*, bonding orbitals,

 $\pi 2p_y$  and  $\pi 2p_x$  have same energy. Similarly  $\pi 2p_y$  and  $\pi 2p_x$  have same energy.

It may be noted that whereas  $\pi 2p_x$  has only one nodal plane, there are two nodal planes in  $\pi 2p_x$  molecular orbital. Similar is the situation with  $\pi 2p_y$  and  $\pi 2p_y$  also.

#### Difference between sigma and pi molecular orbitals

Sigma ( <del>o</del> ) molecular orbital	pi (π) molecular orbital
It is formed by end-to-overlap of atomic orbitals alo the internuclear axis.	It is formed by sidewise overlap of atomic orbitals perpendicular to internuclear axis.
2. The overlapping is maximu	m. The overlapping is comparatively less.
-	to The orbital is not symmetrical to xis. rotation about internuclear axis.
4. It consists of one electron clo	ud. It consists of two electron clouds one above and other below the plane passing through the nuclei.

## Energy Level Diagrams for Molecular Orbitals

The relative energies of molecular orbitals depend on the following factors:

# (i) The energies of the atomic orbitals involved in the formation of molecular orbitals.

For example, pair of molecular orbitals formed by the combination of 2s atomic orbitals will have higher energy than those formed by combination of 1s orbitals. Similarly, molecular orbitals formed by combination of 2p atomic orbitals will have higher energy than those formed by combination of 2s atomic orbitals. Thus,

However, within same pair of molecular orbitals, the bonding molecular orbital has lower energy than the antibonding molecular orbital.

(ii) The extent of overlapping between the atomic orbitals. The greater the overlap, the more the bonding orbital is lowered and the antibonding orbital is raised in energy relative to atomic orbitals. Therefore, the energy of sigma molecular orbital is expected to be lower than pi molecular orbital.

2p orbitals form six molecular orbitals between two atoms.

Bonding orbitals 
$$\sigma 2p_z$$
,  $\pi 2p_x$ ,  $\pi 2p_y$   
Antibonding orbitals  $\sigma 2p_z$ ,  $\pi 2p_x$ ,  $\pi 2p_y$ 

The energy levels of these molecular orbitals have been determined experimentally by spectroscopic methods.

 $\pi 2p_x$  and  $\pi 2p_y$  orbitals have equal energies as these are degenerate orbitals.

 $\mathring{\pi}2p_x$  and  $\mathring{\pi}2p_y$  orbitals have equal energies as these are also degenerate orbitals.

 $\delta 2p_z$  has the maximum energy among the six 2p molecular orbitals.

The energy of  $\sigma 2p_z$  not definite. For diatomic molecules Li<sub>2</sub>, Be<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub> and N<sub>2</sub>, the energy of  $\sigma 2p_z$  is higher than  $\pi 2p_x$  or  $\pi 2p_y$  while for diatomic molecules O<sub>2</sub>, F<sub>2</sub>, Ne<sub>2</sub>, the energy of  $\sigma 2p_z$  is lower than  $\pi 2p_x$  or  $\pi 2p_y$ .

Thus, the energy diagram for first ten molecular orbitals for diatomic homonuclear molecules such as  $\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$  is :

$$\pi 2p_x$$
 $\pi 2p_x$ 
 $\pi 2p_x$ 
 $\pi 2p_x$ 
 $\pi 2p_z$ 
 $\pi 2p_y$ 
 $\pi 2p_y$ 
 $\pi 2p_y$ 

For homonuclear diatomic molecules such as  $O_2$ ,  $F_2$ ,  $Ne_2$ , the energy diagram is:

$$\pi 2p_x$$
  $\pi 2p_x$   $\pi 2p_x$   $\pi 2p_x$   $\pi 2p_z$   $\pi 2p_z$   $\pi 2p_y$   $\pi 2p_y$   $\pi 2p_y$ 

Energy increases

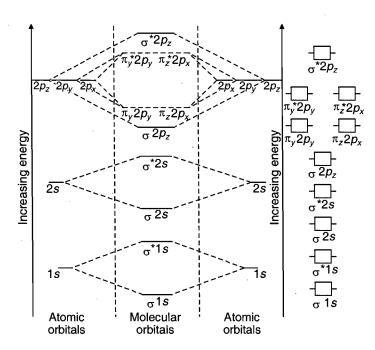


Fig. 2.28 Energy level diagram of molecular orbitals for homonuclear diatomic molecules (O<sub>2</sub>, F<sub>2</sub> and Ne<sub>2</sub>)

## Rules for Filling up of Molecular Orbitals with Electrons

- (i) The molecular orbitals are filled in increasing order of their energy (aufbau principle).
- (ii) The maximum number of electrons which can be accommodated in a molecular orbital is two (Pauli's exclusion principle).
- (iii) If there are two molecular orbitals having the same energy, the electrons will first enter these singly and when both achieve one electron each, pairing will start (Hund's rule).

# Electronic Configuration and Molecular Behaviour

The distribution of electrons among various orbitals is called the electronic configuration. Electronic configuration of the molecule can give the following information about the behaviour of the molecule.

- (i) Stability of molecules: A molecule is formed only when the total energy of the system decreases. This is only possible when bonding electrons are more than antibonding electrons. Suppose the number of electrons present in the bonding orbitals is represented by  $N_b$  and the number of electrons present in the antibonding orbitals  $N_a$ , then
- (a) If  $N_b$  is greater than  $N_a$  ( $N_b > N_a$ ), the molecule is stable. Stability is due to net force of attraction.
- (b) If  $N_b$  is less than  $N_a$  ( $N_b < N_a$ ), the molecule is unstable. Antibonding influence is stronger resulting in a net force of repulsion. This brings instability.

(c) If  $N_b$  is equal to  $N_a$  ( $N_b = N_a$ ), the molecule is unstable. This is because of the fact that the influence of antibonding electrons is slightly more than that of bonding electrons resulting in a net force of repulsion.

#### (ii) Stability in terms of bond order:

Bond order is defined as one half of the difference between the number of electrons present in the bonding and the antibonding orbitals, i.e.,

Bond Order (B.O.) = 
$$\frac{1}{2}$$
(N<sub>b</sub> - N<sub>a</sub>)  
Number of electrons Number of electrons in bonding orbitals – in antibonding orbitals

The bond order provides the following information.

- (a) If the value of bond order is positive, it indicates, a stable molecule or a stable ion. In case, the value of bond order is negative or zero, it indicates that the molecule or ion is unstable or the species does not exist.
- (b) The stability of the bond, *i.e.*, molecule or ion is measured in terms of **bond dissociation energy**. **The bond dissociation energy is directly proportional to the bond order**. Higher is the bond order, greater is the bond dissociation energy, *i.e.*, more is the stability. Thus, a molecule with bond order 3 is more stable than a molecule with a bond order 2 which in turn is more stable than a molecule with a bond order of 1 or  $1\frac{1}{2}$ .
- (c) Bond order 1, 2 and 3 means single, double and triple bonds respectively. [The difference between chemical bond and bond order is that chemical bond is always integral but bond order can be fractional also.]

Bond order Less than zero	Stability The species is highly unstable or does not exist
Zero	The species is highly unstable or does not exist
+ 1/2	The species exists but unstable
+1	A stable single bond
+2	A stable double bond
+3	A stable triple bond

(d) **Bond length is inversely proportional to the bond order.** Greater is the bond order, shorter is the bond length.

Molecule	Bond order	Bond dissociation energy (kJ mol <sup>-1</sup> )	Bond length (pm) <sup>2</sup>
$F_2 (F - F)$	1	158	142
$O_2$ (O = O)	2	497	121
$N_2 (N \equiv N)$	3	945	110

(iii) Magnetic nature: If all the electrons in the molecule or ion are paired, it is diamagnetic in nature. In case, if the molecule has any unpaired electron or electrons, it is paramagnetic in nature. Paramagnetic behaviour depends

upon the number of unpaired electrons, *i.e.*, greater the number of unpaired electrons present in the molecule or ion, greater is the paramagnetic nature. It is expressed in terms of magnetic moment which is equal to  $\sqrt{n(n+2)}$  B.M. Where n is the number of unpaired electrons.

## Molecular Orbital Configurations of Some Homonuclear Diatomic Species

Homonuclear diatomic molecules or ions have two identical atoms linked together. These are  $A_2$  type species.

(i) The hydrogen molecule ion,  $H_2^+$ : This ion has one hydrogen atom and one  $H^+$  ion linked together. Each has 1s-orbital. Using LACO method two 1s-orbitals will combine to give two molecular orbitals.  $\sigma(1s)$  and  $\overset{\star}{\sigma}(1s)$ , the only electron will be accommodated on  $\sigma 1s$ .

Thus, bond order for 
$$H_2^+ = \frac{1}{2}(1-0) = \frac{1}{2}$$

 $H_2^+$  ion can exist but it is unstable. It is paramagnetic in nature. The bond length is 104 pm. Its bond dissociation energy is 269 kJ mol<sup>-1</sup>.

(ii) The hydrogen molecule,  $H_2$ : It is formed from  $1s^1$  atomic orbitals of two atoms. The atomic orbitals  $(1s^1)$  will combine to form two molecular orbitals  $\sigma(1s)$  and  $\dot{\sigma}(1s)$ . Two electrons are accommodated on  $\sigma(1s)$  and  $\dot{\sigma}(1s)$  remains vacant.

Thus, bond order for 
$$H_2 = \frac{1}{2}(2-0) = 1$$

It is stable and diamagnetic in nature. It has single covalent bond. Its bond dissociation energy is 438 kJ mol<sup>-1</sup>. The bond length is 74 pm.

(iii) The hydrogen molecule ion,  $H_2$ : It is formed by linking hydrogen atom with hydrogen ion, H. Both have 1s-orbitals. These will combine to form two molecular orbitals  $\sigma(1s)$  and  $\mathring{\sigma}(1s)$ . These available electrons are accommodated as  $\sigma(1s)^2$  and  $\mathring{\sigma}(1s)^1$ .

Thus, bond order for 
$$H_2^- = \frac{1}{2}(2-1) = \frac{1}{2}$$

It is unstable and paramagnetic in nature.

(iv) Helium molecule,  $He_2^+$ : It is formed by linking helium atom with helium ion,  $He^+$ . Both have 1s-orbitals. These will combine to form two molecular orbitals  $\sigma(1s)$  and  $\sigma(1s)$ . Three electrons are accommodated as  $\sigma(1s)^2$  and  $\sigma(1s)^3$ .

Thus, bond order for 
$$He_2^+ = \frac{1}{2}(2-1) = \frac{1}{2}$$

The value of bond order indicates that  $He_2^+$  can exist but is unstable. The bond dissociation energy is 242 kJ mol<sup>-1</sup>. It is paramagnetic in nature. Both  $H_2^-$  and  $He_2^+$  have same number of electrons in the antibonding orbitals. Both have same stability, similar bond dissociation energy and similar bond lengths.

(v) Helium molecule, He<sub>2</sub>: It is formed by linking two helium atoms. Both have 1s-orbitals. These will combine to form two molecular orbitals  $\sigma(1s)$  and  $\sigma(1s)$ . Four available electrons are accommodated as  $\sigma(1s)^2$  and  $\sigma(1s)^2$ .

Thus, bond order for 
$$\text{He}_2 = \frac{1}{2}(2-2) = 0$$

Hence, there can be no possibility for the existence of  $\text{He}_2$  molecule.

(vi) Lithium molecule, (Li<sub>2</sub>): The electronic configuration of lithium atom (Z = 3) is  $1s^2 2s^1$ . Thus, total number of electrons in Li<sub>2</sub> molecule would be 6. The electronic configuration of Li<sub>2</sub> molecule may be written as:  $\sigma(1s)^2 \sigma(1s)^2 \sigma(2s)^2$ . This may be written as:  $KK [\sigma(2s)^2]$ . Where KK represents fully filled inner K shells in two atoms, *i.e.*,  $[\sigma(1s)^2]$   $[\dot{\sigma}(1s)^2]$ . These are also called non-bonding orbitals.

It is clear from the electronic configuration of  $\text{Li}_2$  molecule that there are 4 bonding electrons and 2 antibonding electrons.

Bond order 
$$=\frac{N_b - N_a}{2} = \frac{4 - 2}{2} = 1$$

Thus, Li<sub>2</sub> molecule is stable. It has one single sigma bond. The bond dissociation energy is 110 kJ mol<sup>-1</sup> and the bond length is 265 pm. As it has no unpaired electron, it is diamagnetic in nature. Li<sub>2</sub> molecules are found to exist in vapour state.

(vii) Be<sub>2</sub>, B<sub>2</sub> and C<sub>2</sub> molecules: The electronic configurations along with bond orders and magnetic nature of these molecules are given below:

Molecule	Total electrons	Configuration	Bond order	Magnetic nature
Be <sub>2</sub>	8	$KK[\sigma(2s)^2] \ [\overset{*}{\sigma}(2s)^2]$	$\frac{1}{2}(4-4)=0$	Does not exist
$B_2$	10	$KK[\sigma(2s)^2] \ [\mathring{\sigma}(2s)^2]$		
C <sub>2</sub>	12	$[\pi(2p_x)^1]$ $[\pi(2p_y)^1]$ $KK[\sigma(2s)^2]$ $[\overset{*}{\sigma}(2s)^2]$	$\frac{1}{2}(6-4)=1$	Paramagnetic
		$[\pi(2p_x)^2]$ $[\pi(2p_y)^2]$	$\frac{1}{2}(8-4)=2$	Diamagnetic

The bond in  $B_2$  is weak  $\pi$  bond. The Bond dissociation energy is 290 kJ mol<sup>-1</sup> and bond length is 159 pm.  $C_2$  molecule has double bond consisting both the  $\pi$  bonds as 4 electrons are present in pi molecular orbitals. Generally, in

most of the molecules, the double bond consists of one sigma and one pi bond. Like  $Li_2$  molecules,  $C_2$  molecules also exist in vapour state.

#### ■ Comparison of stabilities of H<sub>2</sub>, Li<sub>2</sub> and B<sub>2</sub>

The three molecules, *i.e.*,  $H_2$ ,  $Li_2$  and  $B_2$  possess the same value of bond order (*i.e.*, 1) but their stabilities are different.  $H_2$  molecule has maximum stability out of these molecules.

This can be explained as follows:

- (i) Li-Li bond length is much larger than H-H bond length.
- (ii) The overlapping of 2s–2s atomic orbitals in lithium is less effective than the overlapping of 1s–1s atomic orbitals in hydrogen.
  - (iii) Li<sub>2</sub> molecule has two electrons in antibonding orbital while H<sub>2</sub> has no electrons in the antibonding orbital.
- (iv) In Li<sub>2</sub> molecule, the electrons in  $\sigma(2s)$  molecular orbital are shielded by inner  $\sigma(1s)$  electrons. Thus, there is less attraction between electrons in  $\sigma(2s)$  and the nuclei.

Because of above reasons, Li<sub>2</sub> is less stable than H<sub>2</sub>.

Boron atom is smaller in size than Li atom and the  $B_2$  molecule has 6 electrons in the bonding orbitals while  $Li_2$  molecule has four electrons in the bonding orbitals. Hence,  $B_2$  is more stable than  $Li_2$ .

Thus, the order of stability is :  $H_2 > B_2 > Li_2$ 

(viii) Nitrogen molecule (N<sub>2</sub>): The electronic configuration of nitrogen is  $1s^2$ ,  $2s^2 2p^3$ . In nitrogen molecule, there are 14 electrons of which 4 are in the *K* shell and are non-bonding. Each atom contributes four atomic orbitals and thus, the molecule consists of 8 molecular orbitals. Then ten electrons are alloted to molecular orbitals as follows:

$$KK \sigma(2s)^2 \overset{*}{\sigma}(2s)^2 \pi(2p_x)^2 \pi(2p_y)^2 \sigma(2p_z)^2$$

where KK denotes the closed K shell structure  $\sigma(1s)^2 \overset{*}{\sigma}(1s)^2$ .

Bond order = 
$$\frac{1}{2}(8-2) = 3$$
 or =  $\frac{1}{2}(10-4) = 3$ 

Thus, nitrogen molecule has three bonds, one sigma and two pi. The molecule is diamagnetic. It has high bond dissociation energy  $(945 \text{kJ mol}^{-1})$  and bond length is 110 pm.

(ix)  $N_2^+$ ,  $N_2^-$  and  $N_2^2^-$  ions: The configurations of  $N_2^+$ ,  $N_2^-$  and  $N_2^2^-$  ions along with their bond orders, stability and their magnetic character are tabulated below:

· S	pecies	Total electrons	Configurations	Bond order	Stability	Magnetic nature
	N <sub>2</sub>	14	KK $\sigma(2s)^2 \mathring{\sigma}(2s)^2 \pi(2p_x)^2 \pi(2p_y)^2 \sigma(2p_z)^2$	$\frac{(8-2)}{2} = 3$	Most stable	Diamagnetic
	N <sub>2</sub> <sup>+</sup> .	· 13	KK $\sigma(2s)^2 \stackrel{*}{\sigma}(2s)^2 \pi(2p_x)^2 \pi(2p_y)^2 \sigma(2p_2)^1$	$\frac{(7-2)}{2}$ = 2.5	Less stable	Paramagnetic
	$N_2^-$	15	$KK \ \sigma(2s)^2 \stackrel{\star}{\sigma}(2s)^2 \pi(2p_x)^2 \pi(2p_y)^2 \ \sigma(2p_z)^2 \stackrel{\star}{\pi}(2p_x)^1$	$\frac{(8-3)}{2}$ = 2.5	Less stable	Paramagnetic
	$N_2^{2-}$	16	KK $\sigma(2s)^2 \stackrel{*}{\sigma}(2s)^2 \pi(2p_x)^2 \pi(2p_y)^2 \sigma(2p_z)^2 \stackrel{*}{\pi}(2p_x)^1 \stackrel{*}{\pi}(2p_y)^2$	(8-4) = 2	Least stable	Paramagnetic

Bond dissociation energies are directly proportional to the bond orders. The order of bond dissociation energies is :  $N_2 > N_2^+ = N_2^- > N_2^2^-$ . Bond length is inversely proportional to the bond order. The order of bond lengths is:  $N_2^{2^-} > N_2^- = N_2^+ > N_2$ .

(x) Oxygen molecule: The electronic configuration of oxygen is  $1s^2$ ,  $2s^2$   $2p^4$ . In oxygen molecule, there are 16 electrons of which 4 are in the K shell and are non-bonding. Each atom contributes four atomic orbitals and thus, the molecule consists of 8 molecular orbitals. The 12 electrons are alloted to molecular orbitals as follows:

KK 
$$\sigma(2s)^2 \mathring{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \mathring{\pi}(2p_x)^1 \mathring{\pi}(2p_y)^1$$

Note:  $\sigma(2p_z)$  is filled first and then  $\pi(2p_x)$  and  $\pi(2p_y)$  molecular orbitals are filled.

Bond order = 
$$\frac{(8-4)}{2}$$
 = 2

The oxygen molecule has two bonds (one sigma and one pi). The last two molecular orbitals are singly occupied, hence the molecule is paramagnetic in nature. The molecule is stable. The bond dissociation energy is 497 kJ mol<sup>-1</sup> and bond length is 121 pm.

(xi)  $O_2^+$ ,  $O_2^-$  and  $O_2^{2-}$  ions: The configurations of  $O_2^+$ ,  $O_2^-$  and  $O_2^{2-}$  ions along with their bond orders, stability and their magnetic character are tabulated ahead:

Species	Total electrons	Configurations	Bond order	Stability	Magnetic character
O <sub>2</sub>	16	KK $\sigma(2s)^2 \stackrel{\star}{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \stackrel{\star}{\pi}(2p_x)^1 \stackrel{\star}{\pi}(2p_y)^1$	$\frac{(8-4)}{2} = 2.0$	Most stable	Paramagnetic
$O_2^{+}$	15	KK $\sigma(2s)^2 \stackrel{*}{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \stackrel{*}{\pi}(2p_x)^1$	$\frac{(8-3)}{2}$ = 2.5	Most stable	Paramagnetic
$O_2^-$	17	$KK \; \sigma(2s)^2 \stackrel{*}{\sigma}(2s)^2 \; \sigma(2p_z)^2 \; \pi(2p_x)^2 \; \pi(2p_y)^2 \stackrel{*}{\pi}(2p_x)^2 \stackrel{*}{\pi}(2p_y)^1$	$\frac{(8-5)}{2} = 1.5$	- Less stable	Paramagnetic
O <sub>2</sub> -	18	$KK \ \sigma(2s)^2 \stackrel{\star}{\sigma}(2s)^2 \ \sigma(2p_z)^2 \ \pi(2p_x)^2 \ \pi(2p_y)^2 \stackrel{\star}{\pi}(2p_x)^2 \stackrel{\star}{\pi}(2p_y)^2$	$\frac{(8-6)}{2}$ = 1.0	Least stable	Diamagnetic

Bond order

Magnetic

nature

The bond dissociation energies and stability are in the given order:  $O_2^+ > O_2 > O_2^- > O_2^2$ The bond lengths are in the given order:  $O_2^{2-} > O_2^- > O_2^+$ 

(xii) Fluorine molecule: Electronic configuration of F-atom (Z = 9) is  $1s^22s^22p^5$ . Total number of electrons in  $F_2$  molecule is 18 of which 4 are in K shell and are non-bonding. Each atom contributes four atomic orbitals. The 14 electrons are alloted to molecular orbitals as follows:

KK 
$$\sigma(2s)^2 \stackrel{*}{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \stackrel{*}{\pi}(2p_x)^2 \stackrel{*}{\pi}(2p_y)^2$$
  
Bond order =  $\frac{8-6}{2}$  = 1

 $F_2$  molecule has one single bond. The molecule is diamagnetic as no unpaired electron is present in the molecule. The bond dissociation energy is 159 kJ  $\text{mol}^{-1}$  and bond length is 143 pm.

(xiii) Neon molecule (Ne<sub>2</sub>): The electronic configuration of neon atom is  $1s^22s^22p^6$ . In Ne<sub>2</sub> molecule 20 electrons are present, out of which four electrons are in K shell and are non-bonding. The molecular orbital configuration of neon molecule is:

$$KK \, \sigma(2s)^2 \, \mathring{\sigma}(2s)^2 \, \sigma(2p_z)^2 \, \pi(2p_x)^2 \, \pi(2p_y)^2 \, \mathring{\pi}(2p_y)^2 \, \mathring{\pi}(2p_y)^2 \, \mathring{\sigma}(2p_z)^2$$

Bond order = 
$$\frac{8-8}{2}$$
 = 0

Thus, Ne<sub>2</sub> molecule does not exist.

•				•
	O <sub>2</sub>		F <sub>2</sub>	Ne
$\overset{*}{\sigma}(2p_2)$			-	<u>↑↓</u>
$\pi^*(2p_x)$	<u> 1</u>	$\overset{*}{\pi}(2p_y)$	<u> 11 11</u>	<u> </u>
$\pi(2p_x)$	<u> 11 11</u>	$\pi(2p_y)$	<u> </u>	$\uparrow\downarrow\uparrow$
$\sigma(2p_z)$	<u> </u>		. <u>↑↓</u>	$\uparrow\downarrow$
*\sigma(2s)	<u>↑↓</u>	•	<u>11</u>	<u>1</u>
$\sigma(2s)$	<u>1</u> 1		<u> </u>	<u>1</u>
Bond order	2		1	0
Magnetic nature	P		DI	Does not exist

Fig. 2.29 (a) Molecular occupancy of homonuclear diatomic molecules of O<sub>2</sub>, F<sub>2</sub> and Ne<sub>2</sub>

- ·	N <sub>2</sub>	· source	C <sub>2</sub> ·	B <sub>2</sub>
*σ(2 <i>p</i> <sub>z</sub> )		· ·		-
$\pi^*(2p_x)$		$\mathring{\pi}(2p_y)$		
$\sigma(2p_z)$	1	·		
$\pi(2p_x)$	<u> </u>	$\pi(2p_y)$	$\uparrow\downarrow\uparrow\downarrow$	1 1
*\(\sigma(2s)\)	<u>↑↓</u>	·	<u>1</u>	$\uparrow\downarrow$
$\sigma(2s)$	<u> 1</u>		<u>1</u>	<u>1</u>

Fig. 2.29 (b) Molecular occupancy of homonuclear diatomic molecules of B<sub>2</sub>, C<sub>2</sub> and N<sub>2</sub>

Diamagnetic Paramagnetic

### Structures of Heteronuclear Diatomic Molecules

Diamagnetic

The principles involved in the distribution of electrons in the heteronuclear diatomic molecules are the same as in homonuclear diatomic molecules. However, due to the difference in the electronegativity of two atoms, the molecular orbital diagrams will not be symmetrical. The electrons in bonding molecular orbital spend more time near the more electronegative atom. On the other hand, electrons in antibonding molecular orbital are closer to the less electronegative atom. Two examples are discussed below:

#### (i) Nitric oxide molecule (NO):

Total valence electrons = 5 + 6 = 11

The distribution of the electrons in various molecular orbitals of NO molecule is done in the following manner:

KK 
$$\sigma(2s)^2 \stackrel{*}{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \stackrel{*}{\pi}(2p_x)^1$$
  
Bond order =  $\frac{1}{2}(8-3) = 2.5$ 

The presence of one unpaired electron makes the molecule less stable. It is paramagnetic in nature.

Configuration of NO<sup>+</sup> (Valence electrons = 10)

KK 
$$\sigma(2s)^2 \stackrel{*}{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2$$
  
Bond order  $=\frac{1}{2}(8-2)=3$ 

Configuration of NO<sup>-</sup> (Valence electrons = 12)  
KK 
$$\sigma(2s)^2 \, \mathring{\sigma}(2s)^2 \, \sigma(2p_z)^2 \, \pi(2p_x)^2 \, \pi(2p_y)^2 \, \mathring{\pi}(2p_x)^1 \, \mathring{\pi}(2p_y)^1$$
  
Bond order =  $\frac{1}{2}(8-4) = 2$ 

#### (ii) Carbon monoxide molecule (CO):

Total valence electrons = 4 + 6 = 10

The distribution of electrons in various molecular orbitals of CO molecule is done in the following manner:

$$(\sigma 2s)^2 (\mathring{\sigma} 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2$$
  
Bond order =  $\frac{1}{2}(8-2) = 3$ 

It represents one sigma bond and two  $\pi$ -bonds. The molecule is stable and diamagnetic in nature.

#### (iii) CN ion:

Total number of valence electrons = 10The configuration of CN $^{-}$  ion is:

KK 
$$\sigma(2s)^2 \mathring{\sigma}(2s)^2 \pi (2p_x)^2 \pi (2p_y)^2 \sigma (2p_z)^2$$
  
Bond order  $=\frac{1}{2}(8-2)=3$ 

The ion is stable and diamagnetic in nature.

#### (iv) BN molecule:

Total number of valence electrons = 8 The configuration of BN molecule is:

KK 
$$\sigma(2s)^2 \mathring{\sigma}(2s)^2 \pi (2p_x)^2 \pi (2p_y)^2$$
  
Bond order  $= \frac{1}{2}(6-2) = 2$ 

The molecule is stable and diamagnetic in nature.

# Comparison of Valence Bond Theory and Molecular Orbital Theory

#### Points of resemblance

- (i) For the covalent bond formation, orbital overlap is necessary in both the theories.
- (ii) The orbitals responsible for overlapping must have nearly same energies and proper orientation according to both the theories.
- (iii) According to both the theories, the electron density is high in the region between the atomic nuclei.
- (iv) Both the theories account for the directional nature of the bond.
- (v) Both the theories predict the non-existence of He<sub>2</sub> and Ne<sub>2</sub> molecules.
  - (vi) Both the theories are approximate.

#### Points of difference

- (i) In valence bond theory, atomic orbitals of the combining atoms do not lose their individual character to a great extent but in molecular orbital theory atomic orbitals of the combining atoms lose their identity and new molecular orbitals come into existence.
- (ii) According to valence bond theory electron density increases in the region of overlap while in molecular orbital

theory, there is increase as well as decrease in electron density in the region of orbital overlap.

- (iii) In valence bond theory, resonance plays its part while in molecular orbital theory resonance has no role to play.
- (iv) Mathematically, valence bond theory is quite easy to apply while molecular orbital theory is difficult to apply.
- (v) Valence bond theory does not explain paramagnetic nature of  $O_2$  molecule while molecular orbital theory explains the paramagnetic behaviour of  $O_2$  molecule.
- (vi) Valence bond theory fails to explain the existence of  $H_2^+$  ion while molecular orbital theory explains the existence of  $H_2^+$  ion.

## 2.35 METALLIC BONDING

In a metal crystal, one atom is surrounded by 8 or 12 other metal atoms. (This has been shown by X-ray study of metal crystals.) Since, in metals, the valency electrons are few, it is not possible for an atom to form 8 or 12 covalent bonds with neighbouring atoms.

In a metal crystal, all atoms are identical. These atoms cannot be linked by electrovalent bonds as all have same electronegativity. Thus, in metals, the atoms are bonded with each other with a special type of bonding known as metallic bonding. A theory was proposed by Drude in 1900 and modified by Lorentz in 1923, to explain the type of bonding in metals. This theory is known as electron cloud or electron pool or electron-gas theory. Since, the metals are electropositive as the ionisation energies are low, readily lose their valence electrons and converted into positive ions. These electrons move from place to place through the empty valence orbitals of the closed-packed metal ions and are shared simultaneously among all of them. Thus, these electrons link all the atoms together forming a characteristic type of bond, called the metallic bond. As the shared electrons are delocalised, the metallic bond has neither direction nor saturation. There are two essential conditions for metallic bonding. These conditions are:

- (a) The metal atoms should have low ionisation energy.
- (b) There should be sufficient number of vacant orbitals in the valency shell.

The bonding which holds the metal atoms firmly together on account of the force of attraction between metal ions and the mobile electrons is called metallic bonding.

The strength of the metallic bond depends on the number of valency electrons and the charge on the nucleus. As these increase, the metallic bond becomes stronger. It provides an answer to the fact that alkali metals are soft and have low melting and boiling points while transition metals are hard and have high melting and boiling points. The metallic bond is usually a strong bond. This explains the hardness, high melting and boiling points and low volatility of metals. The presence of mobile electrons in the metal crystal explains the main properties of metals such as electrical conductivity, thermal conductivity, metallic lustre, malleability and ductility.

# SOME:SOLVED PROBLEMS

**Problem 1.** (a) Why a molecule is more stable in terms of energy than the uncombined atoms?

#### Solution:

When the atoms combine together to form a molecule, there is always release of energy. Thus, potential energy of a molecule is less than that of uncombined atoms and therefore, the molecule is more stable.

(b) Why sodium chloride does not conduct electricity in solid state but does so in molten state?

#### Solution:

Solid sodium chloride has crystalline structure in which the ions are not free to move. The ions become mobile when it is in molten state and thus, the electricity can be conducted.

(c) Why  $H_2O$  is a liquid while  $H_2S$  is a gas at ordinary temperature?

#### Solution:

Oxygen has high electronegativity than sulphur. As a result,  $H_2O$  forms hydrogen bonding. Consequently, molecules of water come nearer to each other through hydrogen bonding. This results in higher boiling point of water and hence it is a liquid.

(d) The density of ice is less than that of water or ice floats over water. Explain.

#### Solution:

In ice, water molecule is associated with four other molecules through hydrogen bonding in a tetrahedral manner, *i.e.*, it has open-cage like structure in which lesser molecules are packed per mL. When ice melts, the molecules come closer to one another. Consequently the density of water in liquid state is more than in solid state. Thus, ice floats over water.

(e) Methanoic acid, HCOOH, has one carbon-oxygen bond of length 123 pm, and another of 136 pm. Which bond has which length?

#### Solution:

The structure of the molecule is:

The double bonded carbon-oxygen bond is shorter than the other. A double bond between two atoms is always stronger and shorter than a single bond between the same atoms.

(f) Both carbon-oxygen bonds in the methanoate ion, HCOO<sup>-</sup>, have the same length (127 pm). What does this tell about bonding?

#### Solution:

This is due to the presence of resonance in the molecule.

$$H-C \bigcirc O \longrightarrow H-C \bigcirc O$$

Each bond has part of the character of single bond and part of character of a double bond. The electrons are delocalised over the three atoms.

$$H-C\langle O \rangle$$

(g) Water can react with hydrogen ion to make the oxonium ion,  $H_3O^+$ . What is present in water molecule that allows it to react with a hydrogen ion? Describe the bonding in the oxonium ion. Draw a dot and cross diagram for the molecule.

#### Solution:

There are two lone pairs, but only one of them makes a coordinate bond with an empty 1s-orbital on a hydrogen atom.

There are three bonds in the  $\mathrm{H_3O}^+$  ion, all the three are identical but two of them are covalent and one coordinate. The dot and cross diagram is:

**Problem 2.** Draw dot and cross diagrams for the following molecules. Then, use electron repulsion theory to predict their shapes.

(i) CCl<sub>4</sub>, (ii) H<sub>2</sub>S, (iii) NF<sub>3</sub>, (iv) NO, (v) AlCl<sub>3</sub>.

Solution:

(i) CCl<sub>4</sub>

Four bond pairs + no lone pairs = 4 Shape—tetrahedral

(ii) H<sub>2</sub>S



Two bond pairs + two lone pairs = 4
Shape—bent like water

(iii) NF<sub>3</sub>

Three bond pairs + one lone pair = 4 Shape—pyramidal like NH<sub>3</sub>

(iv) NO

Shape—Linear (All diatomic molecules must be linear)

(v) AlCl<sub>3</sub>

Three bond pairs + no lone pair = 3 Shape—triangular planar like BCl<sub>3</sub>

Problem 3. Arrange the following in order of increasing:

- (a) dipole moment H<sub>2</sub>O, H<sub>2</sub>S, BF<sub>3</sub>
- (b) covalent character LiCl, LiBr, LiI
- (c) covalent character NaCl, MgCl2, AlCl3

#### Solution:

(a) BF<sub>3</sub> is a symmetrical molecule. It has zero dipole moment. Oxygen being more electronegative than S, bond moment of O—H is more than S—H. So, the dipole moments are in the order of

$$BF_3 < H_2S < H_2O$$

(b) The anion size in increasing order is

$$Cl^- < Br^- < I^-$$

Hence, LiCl is least covalent and LiI most. The order is

(c) Cation size in decreasing order is

$$Na^{+} > Mg^{2+} > Al^{3+}$$

Thus, Al<sup>3+</sup> ion has maximum polarisation effect and Na<sup>+</sup> ion has least. Thus, the covalent order is

**Problem 4.** Write the electron configurations and calculate the bond order of  $H_2^+$ ,  $H_2$  and  $He_2$ . Explain why bond length in  $H_2^+$  is longer than in  $H_2$ ?

#### Solution:

The number of electrons, their configurations, etc., for the given species are:

Species	No. of electrons	Configuration	N <sub>b</sub>	Na	Bond order $= 1/2[N_b - N_a]$
$H_2^+$	1	(ols)1	1	0	1/2
$H_2$	2	$(\sigma ls)^2$	-2	0	. 1
He <sub>2</sub>	4	$(\sigma ls)^2 (\sigma ls)^2$	2	2	.0.

The bond length in  $H_2^+$  is longer than in  $H_2$  because in  $H_2^+$  only one electron is present to shield the two nuclei from mutual repulsion. In  $H_2$  there are two electrons to hold the two nuclei thus nuclear repulsion is less than that in  $H_2^+$ . Hence, nuclear separation in  $H_2^+$  is more than in  $H_2$ .

**Problem 5.** (a) A diatomic molecule has a dipole moment of 1.2 D. If the bond distance is 1.0 Å, what fraction of an electronic charge, e, exists on each atom?

#### Solution:

Partial charge = 
$$\frac{\text{Dipole moment}}{\text{Bond distance}} = \frac{1.2 \times 10^{-18} \text{ esu cm}}{1.0 \times 10^{-8} \text{ cm}}$$
  
=  $1.2 \times 10^{-10} \text{ esu}$ 

The fraction of an electronic charge

$$= \frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} = 0.25 = 25\% \text{ of } e.$$

(b) The dipole moment of LiH is  $1.964 \times 10^{-29}$  cm and the interatomic distance between Li and H in this molecule is  $1.596 \, \mathring{A}$ . What is the per cent ionic character in LiH?

#### Solution:

The dipole moment of 100% ionic molecule (Li<sup>+</sup>H<sup>-</sup>) = (1 electronic charge) (interatomic distance)

= 
$$(1.602 \times 10^{-19} )$$
 C)  $(1.596 \times 10^{-10} )$  m)

$$= 2.557 \times 10^{-29} \,\mathrm{Cm}$$

Fractional ionic character

Exp. value of dipole moment
Theoretical value of dipole moment
$$= \frac{1.964 \times 10^{-29}}{2.557 \times 10^{-29}} = 0.768$$

The bond in LiH is 76.8% ionic.

**Problem 6.** Interpret the non-linear shape of  $H_2S$  molecule and non-planar shape of  $PCl_3$  using valence shell electron pair repulsion (VSEPR) theory. [I.I.T. 1998]

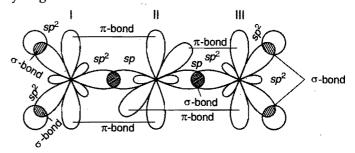
### Solution:

In  $H_2S$ , two bonded pairs and two lone pairs are present, *i.e.*, sulphur is in  $sp^3$  hybridized state. The angle is less than  $109^{\circ}28'$  as contraction occurs due to presence of lone pairs. Thus,  $H_2S$  has V-shaped structure. In  $PCl_3$ , three bonded pairs and one lone pair are present, *i.e.*, phosphorus is also in  $sp^3$  hybridized state but it has pyramidal structure.

**Problem 7.** Discuss the hybridization of carbon atoms in allene  $(C_3H_4)$  and show the  $\pi$ -orbital overlaps. [I.I.T. 1999]

#### Solution:

Allene is  $CH_2$ —C— $CH_2$  carbon atoms I and III are in  $sp^2$  hybridized state while carbon II is in sp hybridized state. Two unhybridized orbitals of carbon II overlap sidewise with unhybridized orbital of each of carbon I and carbon III to form  $\pi$ -bonds besides it also forms a sigma bond with each of the carbon atoms using hybridized orbitals. Two hybridized orbitals of each of carbon I and III form sigma bonds with hydrogen atoms.



**Problem 8.** Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid. [1.1.T. 1999]

Solution: o-hydroxybenzaldehyde show intramolecular hydrogen bonding whereas p-hydroxybenzaldehyde has intermolecular hydrogen bonding. Thus, p-hydroxy-benzaldehyde is an aggregate of a number of molecules and therefore, it is a high melting solid.

$$\bigcirc C = O_{\delta-}$$

$$C = O_{\delta-}$$

$$O = C$$

(o-hydroxybenzaldehyde) Intrahydrogen bonding

Interhydrogen bonding (p-hydroxybenzaldehyde aggregate)

**Problem 9.** In the equation,  $A + 2B + H_2O \longrightarrow C + 2D$  $(A = HNO_2, B = H_2SO_3, C = NH_2OH)$ , identify D. Draw the structures of A, B, C and D. [I.I.T. 1999]

#### Solution:

Solution:

$$HNO_2 + 2H_2SO_3 + H_2O \rightarrow NH_2OH + 2H_2SO_4$$

(A) (B) (C) (D)

Structures—(A) HNO<sub>2</sub>; HO—N=O,

(B) H<sub>2</sub>SO<sub>3</sub>; HO—S→O, (C) NH<sub>2</sub>OH; H—N—OH,

OH O H

(D) H<sub>2</sub>SO<sub>4</sub>; HO—S

**Problem 10.** Write the M.O. electron distribution of  $O_2$ . Specify its bond order and magnetic property.

#### Solution:

O<sub>2</sub> (No. of electrons = 16)  $KK(\sigma 2s)^2 (\sigma^2 2s)^2 (\sigma 2p_z)^2 (\pi 2p_u)^2$  $(\pi 2p_x)^2(\mathring{\pi}2p_y)^1(\mathring{\pi}2p_x)^1$ 

Bond order = 
$$\frac{1}{2}(8-4) = 2$$

As two of the orbitals are singly occupied, the molecule is paramagnetic in nature.

**Problem 11.** Which of the two peroxide ion or superoxide ion has larger bond length?

#### Solution:

The bond length in a molecule is dependent on bond order. The higher is the bond order, smaller will be the bond length. Peroxide ion,  $O_2^{2-}$ 

O<sub>2</sub><sup>2</sup>: 
$$KK(\sigma 2s)^2 (\mathring{\sigma} 2s)^2 (\sigma 2p_z)^2 (\pi 2p_y)^2 (\pi 2p_x)^2 (\mathring{\pi} 2p_y)^2 (\mathring{\pi} 2p_x)^2$$
  
Bond order =  $\frac{8-6}{2}$  = 1

Superoxide ion,  $O_2^-$ 

O<sub>2</sub>: 
$$KK(\sigma 2s)^2(\mathring{\sigma}2s)^2(\sigma 2p_z)^2(\pi 2p_y)^2(\pi 2p_x)^2(\mathring{\pi}2p_y)^2(\mathring{\pi}2p_x)^1$$
  
Bond order =  $\frac{8-5}{2}$  = 1.5

Bond order of superoxide ion is higher than peroxide ion, hence bond length of peroxide ion is larger.

Problem 12. Which d-orbital is involved in hybridization?

#### Solution:

 $d_{x^2-y^2}$ . This is because its four lobes lie along the x-axis and *y*-axis. The two *p*-orbitals can combine along these axes.

**Problem 13.** What is the hybrid state of BeCl<sub>2</sub>? What will be the change in the hybrid state of Be in BeCl<sub>2</sub> in the solid state?

[C.B.S.E. (P.M.T.) 2005]

#### Solution:

In the vapour state, BeCl<sub>2</sub>, exists as a linear molecule, Cl - Be - Cl, i.e., Be is in sp hybridized state. In the solid state, it has a polymeric structure. Each Be atom is linked with 4 Cl atoms, two by covalent bonds and two by coordinate bonds.

Thus, Be atom is in  $sp^3$  hybridized state. Two empty orbitals and two half filled orbitals, i.e., in all four orbitals undergo hybridization.

**Problem 14.** (a) How bond energy varies from  $N_2^-$  to  $N_2^+$  and why?

- (b) On the basis of molecular orbital theory what is similarity between
  - (i)  $F_2$  and  $O_2^{2-}$  (ii)  $CO, N_2, NO^+$ ? [C.B.S.E. (P.M.T.) 2004] Solution:
- (a) Bond energy of  $N_2^+$  = Bond energy of  $N_2^-$  because bond order is same in both the species. [However,  $N_2^+$  is slightly more stable than  $N_2^-$  as antibonding electrons number is higher in  $N_2^-$  than in  $N_2^+$ .]
- (b) (i) Both  $F_2$  and  $O_2^{2-}$  have same bond order same bond length and are diamagnetic.
- (ii) These are isoelectronic species, possess same bond order and same bond length.

Problem 15. Arrange the following compounds in the increasing order of bond length of O—O bond in  $O_2$ ,  $O_2[AsF_6]$ ,  $KO_2$ .

Explain on the basis of ground state electronic configuration of dioxygen in these molecules. [I.I.T. 2004]

#### Solution:

 $O_2[AsF_6]$  has  $O_2^+$  ion while  $KO_2$  has  $O_2^-$  ion.

E.C. of 
$$O_2 = KK\sigma(2s)^2 \mathring{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2$$

$$\pi(2p_x)^1 \pi(2p_y)^1$$

E.C. of 
$$O_2^+ = KK \sigma(2s)^2 \dot{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2$$

E.C. of 
$$O_2^- = KK \sigma(2s)^2 \mathring{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \mathring{\pi}(2p_x)^2 \mathring{\pi}(2p_y)^1$$

B.O. of 
$$O_2 = 1/2 (8-4) = 2$$

B.O. of 
$$O_2^+ = 1/2 (8-3) = 2.5$$

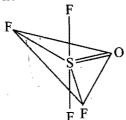
B.O. of 
$$O_2^- = 1/2(8-5) = 1.5$$

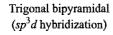
Higher is the B.O., smaller is the bond length. Hence, order of O—O bond length is

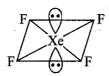
$$O_2^+ > O_2 > O_2^-$$
, i.e.,  
 $O_2[AsF_6] > O_2 > KO_2$ 

**Problem 16.** Using VSEPR, draw the molecular structures of OSF<sub>4</sub> and XeF<sub>4</sub> indicating the position of lone pairs and hybridization of central atoms. [I.I.T. 2004]

#### Solution:







Square planar shape  $(sp^3d^2)$  hybridization

**Problem 17.** Which of the following species have same shape and same bond order?

$$N_3$$
,  $NO_2$ ,  $CO_2$ ,  $O_3$ 

#### Solution:

Isoelectronic species possess same shape and same bond order.

 $CO_2$  and  $N_3$  are isoelectronic = 22 electrons

Similarly,  $NO_2^-$  and  $O_3$  are isoelectronic = 24 electrons

Thus,  $CO_2$  and  $N_3^-$  have same shape and bond order and similarly,  $NO_7^-$  and  $O_3$  have same shape and bond order.

**Problem 18.** Apply VSEPR theory to predict the shapes of  $SF_4$ ,  $ICl_3$ ,  $PbCl_2$  and  $NH_4^+$ .

**Solution:** The Lewis structure of SF<sub>4</sub> is:

S atom is surrounded by five electron pairs (4 bonded and one lone pair) thus, the geometry is trigonal bipyramidal. The actual shape is see-saw.

The Lewis structure of ICl3 is:

Iodine is surrounded by five electron pairs (3 bonded and two lone pairs). Thus, the geometry is trigonal bipyramidal. The actual shape is T-shape.

The Lewis structure of PbCl<sub>2</sub> is:

Pb is surrounded by three electron pairs (2 bonded and one lone pair). Thus, the geometry is trigonal planar. The actual shape is V-shape, *i.e.*, bent structure.



The Lewis structure of NH<sup>+</sup><sub>4</sub> ion is:

$$\begin{bmatrix} H & H \\ H & N & H \\ \bullet & H \end{bmatrix}^{\dagger}$$

Nitrogen is surrounded by four bonded pairs. The shape is thus tetrahedral.

**Problem 19.** Arrange the following in order of (i) increasing N—O bond length (ii) increasing bond angles.

Give reasons.

$$NO_{2}^{+}$$
,  $NO_{2}^{-}$ ,  $NO_{3}^{-}$ 

#### Solution:

Type of hybridization of central atom, *i.e.*, N atom in NO $_2^+$  is sp hybridized while in NO $_2^-$  and NO $_3^-$ , it is  $sp^2$  hybridized. Their structures are:

**Problem 20.** Give reasons for the following observations:

- (a) Sucrose is a covalent compound but it is quite soluble in water.
- (b) Hydrogen bonding does not exist in HCl though chlorine is quite electronegative.
  - (c) o-Nitrophenol has lower boiling point than p-nitrophenol.

#### Solution:

- (a) The molecule of sucrose contains many —OH groups and hence are capable of forming H-bonds with water.
  - (b) This is due to large size of Cl-atom.
- (c) *p*-nitrophenol has higher boiling point due to intermolecular H-bonding.

**Problem 21.** Indicate the type of bonds present in  $NH_4NO_3$  and state mode of hybridization of two N-atoms in it.

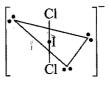
#### Solution:

 $NH_4NO_3$  is an ionic compound in which cation is  $NH_4^+$  ion and anion is  $NO_3^-$  ion. In  $NH_4^+$  ion, three covalent bonds and one coordinate bond is present. The nitrogen is in  $sp^3$  hybrid state, *i.e.*, the species is tetrahedral. In  $NO_3^-$ , nitrogen is in  $sp^2$  hybrid state, *i.e.*, the species is trigonal planar. One oxygen is linked by a double bond, other by a covalent bond and third by a coordinate bond.

**Problem 22.** Explain the shape of  $ICl_{\frac{1}{2}}$  ion.

#### Solution:

Type of hybridization, H = 1/2 [7 + 2 - 0 + 1] = 5, *i.e.*,  $sp^3d$ -hybridization. The central atom 'I' undergoes  $sp^3d$  hybridization. The electron configuration of I-atom in ground state is  $5s^2 5p_x^2 5p_y^2 5p_z^1 5d^0$ . It undergoes hybridization giving five hybrid orbitals. Three hybrid orbitals contain lone pair of electrons each and occupy equatorial positions of the trigonal bipyramid. One hybrid orbital is half filled, it overlaps with an orbital of chlorine atom and forms a covalent bond. One hybrid empty orbital accepts an electron pair from Cl-ion to form a coordinate bond. The Cl-atoms are present on axial positions.





# **SUMMARY AND IMPORTANT POINTS TO REMEMBER**



- 1. A chemical bond is defined as a force that acts between two or more atoms to hold them together as a stable molecule.
- 2. The term valency has been derived from the Latin word 'valentia' which means capacity. Each element was said to have a valency equal to its combining capacity. The number of hydrogen or chlorine atoms with which another atom combines is called its combining capacity. The valency term is now defined as the number of chemical bonds formed by an atom in a molecule. The modern concept believes that electrons are responsible for chemical combination. The atoms interact with each other on account of following reasons:
  - (a) Decrease in energy: Bonded state has lower potential energy than the unbonded state and hence more stable. When two atoms approach the net result should be attraction to form a chemical bond. No chemical bonding is possible if net result is repulsion.
  - (b) Lewis octet rule: The noble gases consist of filled outermost shells. Except for helium, whose electronic configuration is  $1s^2$ , the s- and p- subshells of the highest energy level contain a total of eight electrons. The  $s^2p^6$  configuration constitutes a structure of maximum stability and therefore, of minimum energy. The atoms of all elements when enter into chemical combination try to attain noble gas configuration. The tendency to achieve eight electrons in their outermost shell by atoms is known as Lewis octet rule. This is the basis of electronic theory of valency.

- 3. Electronic theory of valency was formulated by Kossel and Lewis and was completed by Langmuir.
  - The union of two or more atoms involving redistribution of electrons in their outershells (either by transference or sharing) in such a way, so that all the atoms acquire stable noble gas configuration of minimum energy is known as electronic theory of valency.

There are two ways by which the atoms can acquire noble gas configuration.

- (a) By losing or accepting electrons
- (b) By sharing electrons.

There are three types of bonds or linkages which hold the atoms together in a molecule.

- (i) Electrovalent bond
- (ii) Covalent bond
- (iii) Coordinate bond.
- 4. The chemical bond formed between two or more atoms as a result of the transfer of one or more electrons from electropositive to electronegative atom is called electrovalent bond. This bond is also called ionic or polar bond.

The bond formed between oppositely charged ions is called electrovalent bond. This bond is not possible between similar atoms.

5. The energy released when the requisite number of positive and negative ions are condensed into crystal to form 1 mole of the compound is called lattice energy. The force of attraction (*F*) between two oppositely charged ions in air with charges

equal to  $q_1$  and  $q_2$  and separated by a distance d is given by,

$$F = \frac{1}{4\pi\varepsilon_0 K} \cdot \frac{q_1 q_2}{d^2} \quad \text{or} \quad F = \frac{1}{4\pi\varepsilon_0 K} \cdot \frac{q_1 q_2}{(r_A^+ + r_B^-)^2}$$

where, K is dielectric constant of medium.

An ionic bond is purely electrostatic in nature. Its formation is favoured by (a) low ionisation potential of electropositive metal (b) high electron affinity of electronegative element and (c) high lattice energy.

The summation of these energies should be negative, i.e., energy is released.

$$I.P. + E.A. + L.E. = -ive$$
 or  $E.A. + L.E. > I.P.$ 

- 6. Compounds having electrovalent bonds are called electrovalent compounds. They have following general properties:
  - (i) Crystalline nature: Electrovalent compounds have closed packed structures and ions have no freedom of movement. These are not found in liquid or gaseous states under ordinary conditions of temperature and pressure and exist as solids. They have low volatility and high stability. They have high density and high melting and boiling points.
  - (ii) Hard and brittle
  - (iii) Fairly soluble in polar solvents and insoluble in non-polar solvents
  - (iv) Electrovalent solids do not conduct electricity
  - (v) Do not show stereo-isomerism
  - (vi) Show ionic reactions.
- 7. Variable electrovalency: Certain elements show more than one electrovalency in their electrovalent compounds. The following are two reasons for variable valency:
  - (a) Instability of the core: The residue configuration left after the loss of valency electrons is called a core or kernel. In the case of the atoms of transition elements, ions formed after the loss of valency electrons do not possess a stable core as the configuration of the outermost shell is not ns²np6 but ns²np6nd¹-10. This shell generally loses one or more electrons giving rise to metal ions of higher valencies.
  - **(b) Inert pair effect**: Some of the heavier representative elements of third, fourth and fifth groups having configurations of the outermost shell  $ns^2np^1$ ,  $ns^2$   $np^2$  and  $ns^2np^3$  show valencies with a difference of 2, *i.e.*, (1; 3), (2; 4), (3; 5) respectively. The reluctance of *s*-electron pair to take part in bond formation is known as inert pair effect.
- 8. Covalent bond: The second mode of combination was first proposed by Lewis in 1916. There are atoms which attain noble gas configuration by sharing one or more electron pairs when each atom contributes equally. The pair or pairs of electrons become a common property of both. Such a bond is possible between similar and dissimilar atoms. In this bond atoms do not acquire any charge. The electrons which are shared, occupy such a position in between the nuclei of the two atoms where there is maximum force of attraction from

- the two nuclei. The bond is termed a non-polar bond. Covalent bond may be single, double or a triple bond. Double and triple covalent bonds are called multiple covalent bond.
- O. Covalency: It is defined as the number of electrons contributed by an atom of the element for sharing with other atoms as to achieve noble gas configuration. The usual covalency of an element except hydrogen is equal to (8–group number to which the element belongs in Mendeleev's periodic table). This is true for 4th, 5th, 6th and 7th group elements. Generally, the covalency of an element is equal to the number of unpaired electrons in s- and p- orbitals of the valency shell. The elements having vacant d-orbitals in their valency shell like P, S, Cl, Br, I show variable covalency by increasing the number of unpaired electrons under excited conditions.
- 10. Covalent compounds: The compounds containing a covalent bond or a number of covalent bonds are termed covalent compounds. The characteristics of the covalent compounds are:
  - (i) These exist as gases or liquids under normal conditions as very weak attractive forces exist between the molecules, some exist as soft solids if the molecular masses are high.
  - (ii) With the exception of few having giant structures, others have relatively low melting and boiling points.
  - (iii) Covalent compounds are, in general, bad conductors of electricity.
  - (iv) Covalent compounds are insoluble in polar solvents and soluble in non-polar solvents. This is based on the principle 'Like dissolves like'.
  - (v) Show molecular reactions.
  - (vi) The covalent bond is rigid and directional. Covalent compounds show isomerism.
- 11. Coordinate bond is a special type of covalent bond. It is defined as a covalent bond in which both electrons of the shared pair are contributed by one of the two atoms. Such a bond is also called as dative bond. This bond is established between two such atoms, one of which has a complete octet and possesses a pair of valency electrons (donor) while the other is short of a pair of electrons (acceptor). The properties of coordinate compounds are intermediate between the properties of covalent compounds and electrovalent compounds.
- 12. There are several stable molecules such as BeCl<sub>2</sub>, BF<sub>3</sub>, PCl<sub>5</sub>, SF<sub>6</sub>, IF<sub>7</sub>, etc., in which octet rule is violated, *i.e.*, atoms in these molecules are either short of octet (less than 8 electrons in the valency shell) or more than octet.
- 13. Lewis dot formulae are used to represent atoms covalently bonded in a molecule or a polyatomic ion. Lewis dot formulae show only the number of valency electrons, the number and kinds of bonds but do not depict the three dimensional shapes of molecules and polyatomic ions. The formal charge on the atoms in a Lewis dot structure of a molecule or polyatomic ion can be calculated by the application of following formula:

Formal charge on = total number of valency electrons an atom in the free atom – total number of non-bonding electrons – 1/2 total number of bonding shared electrons

14. A covalent bond, in which electrons are shared unequally and the bonded atoms acquire a partial positive and negative charge is called a polar covalent bond. Bond polarity is described in terms of ionic character which usually increases with increasing difference in the electronegativity between bonded atoms.

Percentage of ionic character =  $[16 (X_A - X_B) + 3.5 (X_A - X_B)^2]$  where  $X_A$  and  $X_B$  are electronegativity of atoms A and B. 50% ionic character corresponds to  $(X_A - X_B)$  equal to 2.1.

15. The polarity of the molecule is indicated in terms of dipole moment. Dipole moment is defined as the product of the distance separating charges of equal magnitude and opposite sign with the magnitude of the charge.

 $\mu$  = electric charge × bond length =  $q \times d$ 

Dipole moment is measured in 'Debye' unit (D).  $1D = 10^{-18}$  esu cm =  $3.33 \times 10^{-30}$  coulomb metre. The value of dipole moment increases as the electronegativity difference in diatomic molecule increases. Greater the value of dipole moment of the molecule, greater the polarity of the bond between the atoms. The overall dipole moment of a polar molecule depends on the geometry and shape of the molecule.

Linear molecules like  $CO_2$ ,  $CS_2$ ,  $BeF_2$  and symmetrical molecules like  $BF_3$ ,  $CH_4$ ,  $CCl_4$ , etc., have zero dipole moment. Percentage of ionic character in a bond

= Experimental value of dipole moment × 100 Theoretical value of dipole moment

16. The attractive force that binds hydrogen atom of one molecule with electronegative atom of the other molecule of the same or different substance is known as hydrogen bond. Hydrogen bonding occurs when H-atom is linked to F, O or N atoms (i.e., with small size and high electronegativity). H-bond is usually longer than the covalent bond present in the molecule. Bond energy of hydrogen bond is in the range of 3 to 10 kcal mol<sup>-1</sup> (10 to 40 kJmol<sup>-1</sup>), i.e., about 1/10 the energy of the covalent bond. Hydrogen bond strength increases with the increase in electronegativity and decrease in size of the atom.

$$H - F - - H > H - O - - H > H - N - - - H$$

Hydrogen bond never involves more than two atoms. All the three atoms X—H---X lie in the straight line.

- 17. (a) In water, each O-atom is linked with four H-atoms, two by covalent bonds and two by hydrogen bonds.
  - (b) HF<sub>2</sub> (or KHF<sub>2</sub>) exists but HCl<sub>2</sub> (or KHCl<sub>2</sub>) does not because there is hydrogen bonding in HF but not in HCl.
  - (c) Cl has same electronegativity as N, yet there is no H-bonding in HCl because size of Cl is large.
  - (d) Intermolecular H-bonding results in increase in melting

- and boiling points whereas intramolecular H-bonding results in decrease in melting and boiling points.
- (e) Ice has maximum density at 4°C (277K).
- 18. When anions and cations approach each other, the valence shells of the anions are pulled towards cation nucleus and thus, the shape of anion is deformed. This phenomenon of deformation of anion by a cation is known as polarization and the ability of the cation to polarize a nearby anion is called as polarizing power of the cation.

Fajan observed that greater the polarization of the anion in the molecule, more is the covalent character in it.

- 19. Valence bond theory: This theory was presented by Heitler and London in 1927 to explain how a covalent bond is formed. The theory was extended by Pauling and Slater in 1931. The main points of the theory are:
  - (i) A covalent bond is formed by overlapping of atomic orbitals of valency shell of two atoms.
  - (ii) Only half filled atomic orbitals, i.e., orbitals singly occupied with opposite spins can enter into overlapping process. The resultant bond acquires a pair of electrons with opposite spins.
  - (iii) The atoms with half filled orbitals must come closer to one another with their axes in proper directions for overlapping.
  - (iv) As a result of overlapping, there is maximum electron density somewhere between the two atoms.
  - (v) Greater the overlapping, higher is the strength of the chemical bond. The amount of energy released per mole during overlapping is termed bond energy. This energy stabilizes the system.
  - (vi) Greater the overlapping, lesser will be the bond length.
  - (vii) Electrons which are already paired in valency shell can enter into bond formation if they can be unpaired first and shifted to vacant orbitals.
  - (viii) Two types of bonds are formed. These are (a) sigma (σ) and (b) pi (π) bond. Bond orbital which is symmetrical about the line joining the two nuclei is known as sigma bond. It is formed by head on or axial overlap. π-bonds are formed by the sidewise or lateral overlapping of p-orbitals.

 $\pi$ -bond is a weaker bond in comparison to sigma bond. The bond orbitals lie below and above the internuclear axis.  $\pi$ -bonds are formed only when  $\sigma$ -bond has already been formed.  $\pi$ -bonds are more reactive than sigma bonds. The shape of the molecule is decided by  $\sigma$ -bonds.  $\pi$ -electrons are mobile in nature. A double bond consists one  $\sigma$ -bond and one  $\pi$ -bond while a triple bond consists one  $\sigma$ -bond and two  $\pi$ -bonds. All single bonds are sigma bonds.

Bond strength : Single bond < Double bond < Triple bond Bond length : Single bond > Double bond > Triple bond Reactivity : Single bond < Double bond < Triple bond

20. Hybridization: The valence bond theory explains satisfactorily the formation of various molecules but fails to account the geometry and shapes of various molecules. Hybridization is a hypothetical concept. The process of mixing or amalgamation of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy is known as hybridization.

Number of hybrid orbitals formed = number of atomic orbitals mixed

Most of the hybrid orbitals are similar but they are not necessarily identical in shape. They never form  $\pi$ -bonds.

21. Type of No. of hybrid Shape of molecule Bond angle Examples hybridization orbitals 2 Linear N<sub>2</sub>O, [Ag(CN)<sub>2</sub>]<sup>-</sup>, BeCl<sub>2</sub>, BeF<sub>2</sub>, CO<sub>2</sub>, CS<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, HgCl<sub>2</sub>, HCN sp $sp^2$ BF<sub>3</sub>, BCl<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>, CO<sub>3</sub><sup>2</sup>, SO<sub>3</sub>, NO<sub>3</sub>, ČH<sub>3</sub> 3 Triangular planar  $sp^3$ CH<sub>4</sub>, CCl<sub>4</sub>, SiF<sub>4</sub>, NH<sub>4</sub>, SO<sub>4</sub><sup>2</sup> 4 **Tetrahedral** 109.5°  $dsp^2$ [PtCl<sub>4</sub>]<sup>2-</sup>, [Ni(CN)<sub>4</sub>]<sup>2-</sup> 4 Square planar 90° dsp<sup>3</sup> or sp<sup>3</sup>d 5 Trigonal bipyramidal 120° and 90° PCl<sub>5</sub>, PF<sub>5</sub>, [Fe(CO)<sub>5</sub>]  $d^2sp^3$  or  $sp^3d^2$ 6 Octahedral 90° SF<sub>6</sub>, UF<sub>6</sub>, TeF<sub>6</sub>  $d^3sp^3$  or  $sp^3d^3$ 7 Pentagonal bipyramidal 72° and 90° · IF<sub>7</sub>

Hybridization and Structures of Molecules having Lone Pair or Pairs

Type of molecule			Hybridization	Bond angle	Expected geometry	Actual geometry (shape)	Examples
AX <sub>2</sub>	2	1	$sp^2$	<120°	Trigonal	V-shaper or	SO <sub>2</sub> , SnCl <sub>2</sub> ,
					planar	Bent molecule	PbCl <sub>2</sub> , NO <sub>2</sub> <sup>+</sup>
$AX_2$	2	2	$sp^3$	<109°28'	Tetrahedral	V-shape	H <sub>2</sub> O, H <sub>2</sub> S, NH <sub>2</sub> , SCl <sub>2</sub> , OF <sub>2</sub> ,
							Cl <sub>2</sub> O, H <sub>2</sub> Se, ClO <sub>2</sub> , ClOF
$AX_2$	2	3	sp <sup>3</sup> d	180°	Trigonal	Linear	XeF <sub>2</sub> , I <sub>3</sub> , ICl <sub>2</sub>
					bipyramidal		
$AX_3$	3	2	sp <sup>3</sup> d	90°	Trigonal bipyram	idal T-shaped	ClF <sub>3</sub> , ICl <sub>3</sub> , BrF <sub>3</sub> , XeOF <sub>2</sub>
$AX_3$	3	1	$sp^3$	<109°28'	Tetrahedral	Pyramidal	NH <sub>3</sub> , PH <sub>3</sub> , PCl <sub>3</sub> , BiCl <sub>3</sub> , AsCl <sub>3</sub> ,
	•						$NF_3$ , $PF_3$ , $XeO_3$ , $CIO_3^-$ , $SO_3^{2-}$
						•	P(CH <sub>3</sub> ) <sub>3</sub> , H <sub>3</sub> O <sup>+</sup>
$AX_4$	4	1	sp <sup>3</sup> d	120°, 90°	Trigonal	Trigonal	SF <sub>4</sub> , SCl <sub>4</sub> , TeCl <sub>4</sub> , XeO <sub>2</sub> F <sub>2</sub>
			•		bipyramidal	pyramidal	
$AX_4$	4	2	$sp^3d^2$		Octahedral	Square	XeF <sub>4</sub> , ICl <sub>4</sub>
-			•			planar	• •
$AX_5$	5	1	$sp^3d^2$	<90°	Octahedral	Square pyram	idal IF <sub>5</sub> , BrF <sub>5</sub> , SbF <sub>5</sub> <sup>2</sup>
$AX_6$	6	1	$sp^3d^3$		Pentagonal	Distorted	* XeF <sub>6</sub> , SF <sub>6</sub>
-			•		pyramidal	Octahedral	•

- 22. (a) The hybridization of carbon in CH<sub>4</sub>,  $C_2H_4$  and  $C_2H_2$  is  $sp^3$ ,  $sp^2$  and sp respectively. The bond angles are 109.5°, 120° and 180° respectively.
  - (b) The hybridization of O-atom in  $H_2O$  and that of N-atom in ammonia is  $sp^3$ . The shape of  $H_2O$  is V-shape (bent molecule) while that of NH<sub>3</sub> is pyramidal. The bond angles are 104.5° and 106.5° respectively.
  - (c) The hybridization of O-atom in  $H_3O^4$  ion and that of N-atom in  $NH_4^+$  ion is  $sp^3$ . The shape of  $H_3O^+$  is pyramidal while that of  $NH_4^+$  is tetrahedral.
  - (d) The percentage of s-character in  $sp^3$ ,  $sp^2$  and sp is 25%, 33% and 50% respectively. Order of size of orbitals :  $sp < sp^2 < sp^3$ .
  - (e) Diamond involves  $sp^3$  hybridization. It is hard and a bad conductor of electricity. Graphite involves  $sp^2$  hybridization. It is soft and a good conductor of electricity.
- 23. If two or more alternate valence bond structures can be written for a molecule, the actual structure is said to be a resonance or mesomeric hybrid of all these alternate structures. Actually resonance hybrid does not oscillate between the various

mesomeric forms but it is a definite form and has a definite structure which cannot be written on paper.

Resonance hybrid has lower energy than any of contributing structures and hence is more stable. Resonating structures should have same position of atoms, same number of paired and unpaired electrons, almost equal energy. They differ only in the arrangement of electrons with a restriction that like charges should not reside on atoms closer together.

- 24. Valence shell electron pair repulsion (VSEPR): The VSEPR model developed by Gillespie and Nyholm in 1957 used for predicting the geometrical shapes of molecules is based on the assumption that electron pairs repel each other and therefore, tend to remain as far apart as possible. The molecular geometry is determined by repulsions between lone pairs and lone pairs; lone pairs and bonding pairs and bonding pairs and bonding pairs. The order of these repulsions is: lp—lp > lp—bp > bp—bp.
- 25. Molecular orbital theory of chemical bonding is more rational and more useful in comparison to valence bond theory. This theory was presented by Hund and Mullikan.

According to this theory, all the atomic orbitals of the atoms participating in molecule formation get disturbed when the concerned nuclei approach nearer. They all get mixed upto give rise to an equivalent number of new orbitals that belong to the molecule now. These are called molecular orbitals. The electrons belonging originally to participating atoms are now considered to be moving along the molecular orbitals under the influence of all the nuclei. The molecular orbitals are, thus, polycentric.

Molecular orbitals of a molecule are obtained by linear combination of atomic orbitals of the bonded atoms. When waves are combined, they may interact either constructively or destructively. When the atomic orbitals overlap in phase, constructive interaction occurs in the region between the two nuclei and a bonding orbital is produced. The energy of bonding orbital is always lower (more stable) than the energies of the combining atomic orbitals. When they overlap out of phase, destructive interference occurs and antibonding orbital is produced. The energy of antibonding orbital is higher (less stable) than the energies of the combining atomic orbitals. The filling of molecular orbitals by electrons follows aufbau principle, Hund's rule and Pauli's exclusion principle. Greek symbols,  $\sigma,\,\pi$  and  $\delta$  are used to denote the molecular orbitals.

The molecular orbitals involved in the formation of most of the molecules are:

Bonding orbitals  $\sigma$ 1s o

σ1s σ2s σ2
$$p_z$$
 π2 $p_y$  π2 $p_x$ 

Antibonding orbitals  $\mathring{\sigma}1s \, \mathring{\sigma}2s \, \mathring{\sigma}2p_z \, \mathring{\pi}2p_y \, \mathring{\pi}2p_x$ 

The sequence of molecular orbitals on the basis of energy for  $O_2$ ,  $F_2$  and  $Ne_2$  molecules is:

$$\sigma_{1s} < \dot{\sigma}_{1s} < \sigma_{2s} < \dot{\sigma}_{2s} < \sigma_{2p_z} < \frac{\pi^2 p_y}{\pi^2 p_x} < \frac{\pi^2 p_y}{\pi^2 p_x} < \pi^2 p_z$$

and the sequence of molecular orbitals for  $B_2$ ,  $C_2$ ,  $N_2$  molecules is:

$$\sigma 1s < \dot{\sigma} 1s < \sigma 2s < \dot{\sigma} 2s < \frac{\pi}{\pi} 2 p_y < \sigma 2 p_z < \frac{\pi}{\pi} 2 p_y < \dot{\sigma} 2 p_z$$

The maximum number of electrons which can be accommodated in a molecular orbital is two. If there are two molecular orbitals having same energy, the electrons will first enter these singly and both of them have achieved one electron each, pairing will start.

A molecule is formed only when the total energy of the system decreases. This is only possible when the bonding electrons are more than antibonding electrons.

The number of covalent bonds in a molecule is indicated by bond order.

Bond order =

- (a) Greater the bond order of a diatomic molecule or ion, the more stable it will be.
- (b) Greater bond energy indicates the greater stability of the bond.
- (c) Fractional bond order indicates ion.
- (d) Negative bond order is impossible. It rather indicates instability. The species does not exist.
- (e) Zero bond order also indicates that species does not exist.26. According to 'electron sea model' of metallic bond, metal

consists of positively charged ions called kernels in a sea of mobile electrons. The metallic bond is formed due to simultaneous attraction of mobile electrons by the kernels. According to 'valence bond model' or 'resonance model' the covalent bond present between metal atoms resonates among the neighbouring metal atoms.

According to 'bond model' or 'molecular orbital approach' atomic orbitals merge to form energy bonds. A substance is a conductor when the electrons can be readily promoted to the conduction band where they are free to move through the substance. In insulators, the energy gap between the valence band and the conduction band is so large that the electrons cannot be promoted to the conduction band. In semiconductors, electrons can cross the energy gap at high temperatures.

- (a) Isoelectronic species have the same shape and same bond order.
  - (b) The *d*-orbital taking part in  $dsp^2$  hybridization is  $d_{x^2-y^2}$ , in  $sp^3d$  hybridization it is  $d_{z^2}$  and in  $sp^3d^2$ , the two *d*-orbitals involved are  $d_{x^2-y^2}$  and  $d_{z^2}$ . In  $sp^3d^3$  hybridization, the *d*-orbitals involved are  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$ .
  - (c) The bond lengths of O2 and its ions are in the order

$$O_2^{2-} > O_2^- > O_2 > O_2^+$$

as their bond orders are 1, 1.5, 2 and 2.5 respectively.

Bond length 
$$\propto \frac{1}{\text{bond order}}$$

- (d) H-atom always forms sigma bond.
- (e) As the s-character increases in hybridized orbitals, the size becomes smaller of the hybridized orbitals. The bond length decreases while bond energy increases.
- (f) Isosteres are molecules containing same number of atoms and electrons. For example, CO and N<sub>2</sub>.
- (g) There are a number of stable molecules in which the bonds are formed by sharing of an odd number of electrons. Such type of bonds are called odd electron bonds. Some common examples are:

- (h) Electrovalent bonding is strongest while hydrogen bonding is weakest.
- (i) The stability of N<sub>2</sub> and its ions is in the order

$$N_2 > N_2^+ = N_2^- > N_2^{2-}$$

as their bond orders are 3, 2.5, 2.5 and 2 respectively.

(j) Out of  $O_2$ ,  $O_2^+$ ,  $O_2^-$  and  $O_2^{2-}$ , the diamagnetic species is  $O_2^{2-}$ .



## PRACTICE PROBLEM



## **■** Subjective Type Questions

- 1. (a) Write Lewis dot symbols for the following atoms and ions:
  - (i) S and S<sup>2-</sup>
- (ii) Al and Al<sup>3+</sup>
- (iii) Br and Br
- (iv) O and O<sup>2-</sup>
- (v) Sr and  $Sr^{2+}$
- (b) Draw Lewis structures for the following ionic compounds:
  - (i) MgS (ii) AlN
- (iii) CaBr<sub>2</sub> (a) Which one has higher lattice energy?

NaCl or CsCl

- (b) How is lattice energy related with stability of an ionic compound?
- (c) Why are MgO, Al<sub>2</sub>O<sub>3</sub>, etc., used as refractory materials?
- Assign formal charges to each atom in the following structures. Based on formal charges, which is the preferred Lewis structure for the molecule, the dinitrogen monoxide?
  - (a) N = N = 0
- (b) : N = N O:
- (a) Identify the compounds in the following in which S does not obey octet rule.

SO<sub>2</sub>, SF<sub>2</sub>, SF<sub>4</sub>, SF<sub>6</sub>

- (b) Arrange the following in increasing order of dipole moment.
  - (i) CH<sub>3</sub>I, CH<sub>3</sub>Br, CH<sub>3</sub>F, CH<sub>3</sub>Cl
  - (ii) BF<sub>3</sub>, H<sub>2</sub>S, H<sub>2</sub>O
- 5. (a) State whether the following are ionic or covalent:
  - (ii) SnCl<sub>4</sub> (iii) diamond (iv) CaC<sub>2</sub> (i) Na<sub>2</sub>S
  - (v) NaH (vi) C<sub>2</sub>H<sub>4</sub> (vii) CaCl<sub>2</sub> (viii) HCl gas
  - (ix) NH<sub>4</sub> (x) KBr
  - (b) Indicate whether the following pairs of elements form ionic or covalent compounds and write down the molecular formula of the compound formed.
    - (i) sodium and chlorine (ii) carbon and sulphur
    - (iii) sulphur and oxygen (iv) calcium and hydrogen
  - (c) What type of bonds are present in the following molecules?
    - (i) MgF<sub>2</sub> (ii) BrCl (iii) CBr<sub>4</sub> (iv) C<sub>2</sub>N<sub>2</sub> (v) CuS
    - (vi) H<sub>2</sub>O (vii) H<sub>2</sub>SO<sub>4</sub>
- (viii) SO<sub>2</sub> (ix) HNO<sub>3</sub>
- (x)  $K_4Fe(CN)_6$
- (d) What type of chemical bond is formed between two atoms when:
  - (i) electronegativity difference is zero.
  - (ii) electronegativity difference is small.
  - (iii) electronegativity difference is high.
- 6. (i) Among the following,
  - NaCl, CCl<sub>4</sub>, HCl and CH<sub>4</sub> which is a polar compound?
  - (ii) Which among the following,
    - H<sub>2</sub>O, NH<sub>3</sub>, BF<sub>3</sub> and NH<sub>4</sub> possesses a coordinate bond?
  - (iii) Among the compounds CH<sub>3</sub>COOH, NH<sub>3</sub>, HF and CH<sub>4</sub> in which maximum hydrogen bonding is present?

- (iv) Amongst LiF and LiI which has more covalent character?
- (v) Amongst o-hydroxybenzaldehyde and p-hydroxybenzaldehyde which is more soluble in water?
- (vi) Which among the following have highest lattice energy?

NaCl, KCl, CsCl

(vii) Which one of the following is non-polar?

SO<sub>2</sub>, CHCl<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>

(viii) Which one of the following has strongest bond?

HF, HCl, HBr, HI

- 7. Arrange the following in each as instructed:
  - (i) O, F, S, Cl, N in order of increasing strength of hydrogen bonding (X - - - H - X). [M.L.N.R. 1993]
  - (ii) N2, O2, F2, Cl2 in increasing order of bond dissociation energy.
  - (iii) NO<sub>2</sub>, NO<sub>2</sub>, NO<sub>3</sub> in order of increasing N—O bond length. [M.L.N.R. 1993]
  - (iv) C—C, C=C, C≡C in order of increasing bond energy.
  - (v) C—C, C=C, C≡C in order of increasing bond length.
  - (vi) PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub>, NH<sub>3</sub> in order of increasing polarity.
  - (vii) H2O, NH3, CH4, SF6, BF3, CO2 in order of increasing bond angle.
  - (viii) MgO, CaO, SrO, BaO in order of increasing lattice energy.
  - (ix) Arrange the following in order of increasing bond order,

 $N_2$ ,  $F_2$ ,  $O_2$ ,  $O_2^-$ ,  $O_2^+$ 

- (x) NO, NO<sup>+</sup> and NO<sup>-</sup> in increasing order of bond length.
- Answer the following:
  - (i) How many electron pairs are shared in N2 molecule?
  - (ii) What is the valency of carbon in  $C_2H_4$  and  $C_2H_2$ ?
  - (iii) Which hybridization is predicted for P in PF5 and S in SF<sub>6</sub>?
  - (iv) What types of bonds and how many of each are present in NH<sub>4</sub>?
  - (v) Which hybridization is predicted for Cl in ClF<sub>3</sub>?
  - (vi) Why the bond angle in H<sub>2</sub>O is greater than 90°?
  - (vii) What is the shape of acetylene molecule?
  - (viii) Why zero group elements are inert in nature?
    - (ix) Which type of elements can form electrovalent bond?
    - (x) What type of bond is formed by sharing an electron pair?
  - (xi) Which type of bond exists in molecule NO?
  - (xii) What type of hydrogen bonding exists in liquid water?
  - (xiii) What type of hydrogen bonding exists in orthochlorophenol?
  - (xiv) How many orbitals are singly occupied in O2 molecule?
  - (xv) Why Neon molecule (Ne<sub>2</sub>) is not possible?
  - (xvi) What is magnetic nature of  $O_2^{2-}$  species?

- 9. (a) Two elements *A* and *B* combine to form a compound *AB*. Under what conditions the bond formed will be electrovalent?
  - (b) Two elements A and B combine to form a compound AB. Under what conditions the compound formed will be covalent?
  - (c) Two elements *A* and *B* participate by sharing electrons in chemical bonding. *B* does not contribute any electron of its own. What type of bond is formed?
  - (d) Atoms A, B and C occur in same period and have one, six and seven valence electrons respectively.
    - (i) Will the bond between *B* and *C* predominently ionic or covalent? Explain.
    - (ii) Write the electronic structure of the compound formed between B and C.
    - (iii) Will the bond between *A* and *B* predominently ionic or covalent? Explain.
  - (e) Three elements A, B and C have atomic numbers Z–2, Z and Z+1 respectively. Of these, B is an inert gas.
    - (i) Which one has the highest value of electronegativity?
    - (ii) Which one has the highest value of ionisation potential?
    - (iii) What is formula of compound between A and C?
    - (iv) What will be the nature of the bond between *A* and *C* in the compound formed ?
- 10. (i) Write the two resonance structures of ozone which satisfy the octet rule. [I.I.T 1991]
  - (ii) Write the two resonance structures of  $N_2O$  that satisfy the octet rule. [I.I.T 1990]
  - (iii) Write the resonance structures of carbonate ion.
  - (iv) Write the resonance structures of  $N_3$  ion.
  - (v) Write the resonance structures of NO<sub>3</sub> ion.
  - (vi) Write the resonance structures of SO<sub>4</sub><sup>2</sup>-ion.
- 11. Write down the Lewis formula or electron dot formula of the following compounds:
  - (a) (i)  $SiCl_4$  (ii)  $CO_2$  (iii)  $PO_4^3$  (iv)  $H_2O_2$
  - (b) (i)  $O_3$  (ii)  $COCl_2$  (iii)  $N_2O_5$  (iv)  $S_2O_3^2$ 
    - (v)  $ClO_3^-$  (vi) CO (vii)  $SO_2Cl_2$  (viii)  $P_2O_7^4$
    - (ix)  $N_2O_4$  (x)  $NH_4^+$
- **12.** Write down the hybridization of the central atom and geometry of the following molecules or ions:
  - (a)  $I_3^-$  (b)  $PbCl_4$  (c)  $ICl_4^-$  (d)  $XeF_4$  (e)  $BH_4^-$
  - (f) ClF<sub>3</sub> (g) HOCl.
- **13.** (a) Which of the following species has greater polarising power?
  - (i)  $Fe^{3+}$  or  $Fe^{2+}$  (ii)  $Cu^{+}$  or  $Na^{+}$  (iii)  $Mg^{2+}$  or  $Al^{3+}$
  - (b) Which of the following species will be most susceptible to polarisation?
    - (i)  $Br^-$  or  $I^-$  (ii)  $O^{2-}$  or  $S^{2-}$  (iii)  $N^{3-}$  or  $O^{2-}$
  - (c) Which compound of each of the following pairs is more covalent?
    - (i) CuO or CuS
- (ii) AgCl or AgI

- (iii) PbCl2 or PbCl4
- (iv) AlCl3 or GaCl3
- (v) LiCl or KCl
- (vi) BeCl2 or MgCl2
- (d) Which of the following pairs of bonds contain the larger ionic contribution to the bonding?
  - (i)  $K^+-F^-$  or  $K^+-I^-$  (ii)  $Na^+-O^{2-}$  or  $Mg^{2+}-O^{2-}$
- (e) Which of the following species has higher melting point?
  - (i) NaCl or CuCl
- (ii) CaF<sub>2</sub> or CaI<sub>2</sub>
- (iii) CaCl<sub>2</sub> or CdCl<sub>2</sub>
- 14. (a) What type of bond is normally expected between:
  - (i) a small cation and large anion.
  - (ii) two electronegative atoms.
  - (iii) a highly electropositive and highly electronegative atoms.
  - (iv) an atom with a completed octet and an atom with a sextet of electrons?
  - (b) Give one example of each:
    - (i) A molecule with central atom devoid of octet.
    - (ii) A molecule with linear shape.
    - (iii) An ionic compound insoluble in water.
    - (iv) Almost a non-polar covalent compound between two different atoms.
    - (v) A stable compound formed by combination of two stable compounds through coordination.
    - (vi) A compound which is bad conductor in gaseous state but its aqueous solution is a good conductor of current.
    - (vii) A compound whose central atom undergoes  $sp^3$  hybridization possesses bond angle about 106.5°.
  - (c) (i) Which one of them is more ionic and why? LiC.
    NaCl
    - (ii) Which one of them is having higher melting point and why? AlCl<sub>3</sub>, MgCl<sub>2</sub>
    - (iii) Which one of them is a good conductor of electricity and why? NaCl, CH<sub>4</sub>
    - (iv) Which one of them is pyramidal and why? BCl<sub>3</sub>, NH<sub>3</sub>
    - (v) Which one of them is a liquid and why? HF, H<sub>2</sub>S
- 15. Explain with suitable examples or write short notes on:
  - (i) Electrovalency
- (ix) Octet rule
- (ii) Covalency
- (x) Dipole moment
- (iii) Coordinate valency(iv) Hydrogen bonding
- (xi) Hybridization(xii) Fajan's rules
- (v) Metallic bonding
- (xiii) Sigma and  $\pi$ -bonds
- (vi) Variable valency
- (xiv) Bond order
- (vii) Inert pair effect
- (xv) Lattice energy
- (viii) Resonance
- (xvi) Polar and non-polar bonds
- 16. Give reasons for the following:
  - (i) The boiling point of ethyl alcohol is much higher than that of diethyl ether.
    - [Hint: Hydrogen bonding is present in alcohol. It is an associated liquid. No hydrogen bonding is present in diethyl ether.]
  - (ii) BCl<sub>3</sub> and BF<sub>3</sub> are non-polar.
    - [Hint: Both are triangular planar and symmetrical molecules. Their dipole moments are zero.]

(iii) Water is good solvent for ionic compounds.

[Hint: Water has high dielectric constant and polar in nature. These properties help in the ionisation of ionic compounds.]

(iv) MgCl<sub>2</sub> is linear but SnCl<sub>2</sub> is angular.

[M.L.N.R. 1995]

[Hint: In MgCl2, Mg is sp hybridized while in SnCl2, Sn is sp<sup>2</sup> hybridized.]

(v) NCl<sub>5</sub> does not exist while PCl<sub>5</sub> does.

[Hint: In N-atom d-orbitals are not present while in P-atom d-orbitals are present and ns electron can be shifted to nd-orbital.]

(vi) Lead prefers to form divalent compounds.

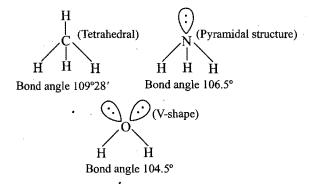
[Hint: ns2 pair of electrons inert and only two electrons of np-orbitals participate. This is due to inner penetration of ns-orbital.]

(vii) Sigma bond is more stronger than  $\pi$ -bond.

[Hint: In sigma bond greater overlapping takes place.]

(viii) CH<sub>4</sub>, NH<sub>3</sub> and H<sub>2</sub>O contain same number of electrons but their shapes are different.

[Hint: The central atom in each of the three molecules CH4, NH<sub>3</sub> and H<sub>2</sub>O undergoes sp<sup>3</sup> hybridization. In CH<sub>4</sub>, no lone pair is present. In NH3 one lone pair is present while in water two lone pairs are present.]



(ix) Calcium fluoride is more ionic than Cal<sub>2</sub>.

[Hint: The size of I ion is bigger than F ions. In CaI2, therefore, more polarisation is present. Thus, CaF2 is more ionic than Cal2.]

(x) Ammonium salts are much more soluble in water than the corresponding sodium salts.

[Hint: Na+ ion is solvated by ion-dipole interaction while NH<sub>4</sub> ion is solvated by H-bonding which is a stronger attractive force.]

(xi) Carbon has two electrons in the outermost, but it is tetravalent in organic compounds.

[Hint: Since, all the four valencies of carbon are identical, 2s electron is shifted to one of the vacant p-orbital with the result four unpaired orbitals are present. These undergo hybridization and form four hybrid

(xii) Why BeF<sub>2</sub> and BF<sub>3</sub> are stable though Be and B have less than 8 electrons? Which one is more stable?

[Hint: The stability is explained by symmetrical linear structure for BeF2 and triangular planar structure for BF3. BeF2 is more stable because of its greater bond angle (180°).]

(xiii) Though the electronegativities of nitrogen and chlorine are same, NH3 exists as liquid whereas HCl as gas. Why?

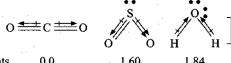
[Hint: The size of nitrogen is less than the size of chlorine. Therefore, electron density in nitrogen is more than that of chlorine. So, nitrogen forms hydrogen bonding leading to association of molecules. Hence, NH3 is a liquid. Hydrogen bonding is not possible with chlorine.]

(xiv) Why the repulsions between non-bonded orbitals are greater than between the bonded orbitals?

[Hint: The non-bonded orbitals relatively occupy more space compared to the bonded orbitals and thus repulsions are greater.]

(xv) Although CO2 has no dipole moment, SO2 and H2O have considerable dipole moments.

[Hint: CO2 has linear structure while SO2 and H2O have V-shaped structures.]



Dipole moments

(xvi) Nitrogen trifluoride (NF3) and ammonia (NH3) have identical shape and a lone pair of electrons on nitrogen and further the electronegativity difference between the elements is nearly the same but the dipole moment of NH<sub>3</sub> is very high in comparison to NF<sub>3</sub>.

> [Hint: It is due to different directions of moments of the N-H and N-F bonds.]

(xvii) Although formation of NH3 and H2O molecules involve  $sp^3$  hybridization, their bond angles are shorter than the normal tetrahedral angle.

> [Hint: This is due to the presence of one lone pair of electrons on nitrogen atom in NH3 and two lone pairs of electrons on oxygen atom in H2O.]

(xviii) Bond order in N2 is 3 whereas it is 2.5 in NO.

[M.L.N.R. 1994]

[Hint:  $N_2 = (\sigma 1s)^2 (\tilde{\sigma} 1s)^2 (\sigma 2s)^2 (\tilde{\sigma} 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y)^2 (\pi 2p_z)^2$ 

Bond order = 
$$\frac{1}{2}(10 - 4) = 3$$

NO =  $(\sigma 1s)^2 (\overset{*}{\sigma} 1s)^2 (\sigma 2s)^2 (\sigma 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y)^2 (\pi 2p_z)^2 (\overset{*}{\pi} 2p_y)^1$ 

**Bond** order = 
$$\frac{1}{2}(10 - 5) = 2.5$$
]

- (xix) Three carbon-oxygen bonds are equal in carbonate ion. [Hint: The carbonate ion exhibits resonance and therefore, all the three C-O bonds are equal.]
- (xx) Valency of oxygen is generally two whereas sulphur shows valency of two, four and six.

[Hint: There are no d-orbitals in oxygen hence it cannot extend its covalency. Vacant d-orbitals are present in sulphur and paired orbitals can be unpaired by shifting electrons to d-orbitals, i.e., either making four orbitals singly occupied or six orbitals singly occupied showing valency 4 or 6 besides 2.]

(xxi) SnCl<sub>2</sub> is ionic but SnCl<sub>4</sub> is covalent.

[Hint: The size of Sn<sup>4+</sup> ion is smaller than Sn<sup>2+</sup> ion. Hence, polarisation or distortion is more in SnCl<sub>4</sub>, so, it is covalent.]

(xxii) NF<sub>3</sub> is weaker base than NH<sub>3</sub>, NCl<sub>3</sub>, NBr<sub>3</sub> and NI<sub>3</sub>.
[Hint: It is due to larger electronegativity of F-atoms of NF<sub>3</sub>. The lone pair is most difficult to be donated.

(xxiii) BaSO<sub>4</sub> is insoluble in water.

[Hint: Lattice energy is more than hydration energy.]

(xxiv) NO molecule is paramagnetic.

[**Hint**: The molecule contains one unpaired electron in its three electron bond.]

(xxv) Compounds of normal elements are diamagnetic.

[Hint: Normal elements acquire inert gas configuration in compounds, i.e., all the orbitals are doubly occupied and thus, compounds are diamagnetic.]

(xxvi) Anhydrous HCl is bad conductor but in aqueous medium, it is good conductor of current.

[Hint: HCl is a covalent compound and in gaseous state, it does not conduct current. In water, however it reacts to form ions, HCl + H<sub>2</sub>O 

→ H<sub>3</sub>O<sup>+</sup> + Cl<sup>-</sup> and thus conducts current.]

(xxvii) A bond order of 3 is computed for the diatomic molecule. It is possible that in the absence of further information, this triple bond may be made up of two σ-and one π-bonds. Explain.

[Hint: Not possible. The order of filling orbitals and the differentiations existing among bonding, antibonding and non-bonding electrons, never permit the establishing more than one sigma bond.]

(xxviii) Diamond is a hard solid with a very high melting point but a non-conductor of electricity.

[**Hint**: Diamond is a giant molecule–three dimensional figure as every carbon is  $sp^3$  hybridized, *i.e.*, one carbon atom is linked to four other carbon atoms tetrahedrally. Due to continuous covalent bonding all the atoms are held very closely and strongly. As a result, diamond is a very hard solid with high melting point. It is bad conductor as free electrons are not available.]

(xxix) AlCl<sub>3</sub> is largely covalent while AlF<sub>3</sub> is largely ionic. [M.L.N.R. 1995]

[Hint: Due to larger size of Cl<sup>-</sup> ion than F<sup>-</sup> ion, there is greater degree of distortion in AlCl<sub>3</sub>.]

#### 17. Give reasons for the following:

(a) Carbon-oxygen bond lengths in Na<sub>2</sub>CO<sub>3</sub> are equal. [Hint: Bond lengths are equal due to resonance in carbonate ion.]

(b) BeCl<sub>2</sub> has zero dipole moment while SnCl<sub>2</sub> has a dipole moment.

[**Hint**: BeCl<sub>2</sub> has a linear structure while SnCl<sub>2</sub> has angular shape.]

(c) Among planar structures, why the linear structure is more stable than trigonal and square planar?

[Hint: Among planar structures, stability increases with an increase in the bond angle. The bond angle is maximum (180°) in linear structure.]

(d) Why do cotton clothes take a long time to dry as compared to synthetic clothes.

[Hint: Cotton fibres form hydrogen bonds with water molecules.]

(e) Benzene molecule is stable inspite of the fact that it consists of three double bond.

[Hint: Resonance exists in benzene molecule.]

18. Dipole moment of KCl is 3.336 × 10<sup>-29</sup> coulomb metre which indicates that it is highly polar molecule. The interatomic distance between K<sup>+</sup> and Cl<sup>-</sup> in this molecule is 2.6 × 10<sup>-10</sup> m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each molecule. Calculate the percentage of ionic character of KCl.

[Ans.  $4.1652 \times 10^{-29}$  coulomb metre, percentage of ionic character = 80.09]

- 19. The dipole moment of HBr is 2.60 × 10<sup>-30</sup> cm and the interatomic spacing is 1.41 Å. What is the percentage ionic character of HBr?
  [Ans. 11.5%]
- 20. Calculate the percentage of ionic character in K—Cl bond in KCl molecule. The electronegativity values of K and ·Cl are 0.8 and 3.0 respectively.[Ans. 52.1%]
- 21. Calculate the lattice enthalpy of LiF give that the enthalpy of (i) Sublimation of lithium is 155.2 kJ mol<sup>-1</sup>; (ii) Dissociation of 1/2 mole of F<sub>2</sub> is 75.3 kJ; (iii) Ionization energy of lithium is 520 kJ mol<sup>-1</sup>; (iv) Electron gain enthalpy of F(g) is -333 kJ mol<sup>-1</sup>; (v) ΔH<sub>f</sub>° overall is -594.1 kJ mol<sup>-1</sup>.
  [Ans. 1011.6 kJ mol<sup>-1</sup>]

## ■ Matching Type Questions

#### Match the following:

	Match the 10	nownig:			
(A)	(a) C <sub>2</sub> H <sub>2</sub>		(i)	sp <sup>2</sup> h	ybridization
	(b) SO <sub>2</sub>		(ii)	sp <sup>3</sup> d	hybridization
	(c) SO <sub>4</sub> <sup>2-</sup>		(iii)	$sp^3d^2$	hybridization
	(d) $I_3^-$		(iv)	sp hy	bridization
	(e) SF <sub>6</sub>		(v)	sp <sup>3</sup> h	ybridization
	(f) IF <sub>7</sub>		(vi)	$sp^3d^3$	hybridization
(B)	1. BeCl <sub>2</sub>	(i) Pyramidal	(a)	Bond	angle 109°28′
	2. H <sub>2</sub> O (i	ii) Trigonal bipyramid	(b)	Bond	angle 180°
	3. NH <sub>2</sub> (ii	ii) Tetrahedral	(c)	Bond	angle 106.5°
	4. PCl <sub>5</sub> (i				angle 104.5°
	5. CH <sub>4</sub> (	v) Linear	(e)	Bond	angle 90°
	-	i) V-shaped			angle 120°, 90°
(C)	(a) Zero dipo	ole moment		(i)	$C_2H_4$
	(b) Violation	of octet rule		(ii)	$O_2$
	(c) Overlappi	ng concept		(iii)	Kossel and Lewis
	(d) Paramagn	etic molecule		(iv)	Ice
	-	a and one $\pi$ -box	nds		Polar bond
	~	ectric constant			sp <sup>2</sup> hybridization
	-	theory of valer	•		H <sub>2</sub> O
	•	sharing of electr	ons	(viii)	-
	(i) Hydrogen	bonded solid		(ix)	Heitler and
					London
	(j) SO <sub>2</sub>			(x)	PCl <sub>5</sub>

## Auswers

#### Answers: Subjective Type Questions

1. (a) (i) 
$$:\dot{S}:$$
 and  $\left[:\dot{S}:\right]^{2-}$  (ii)  $:\dot{A}!$  and  $\left[Al\right]^{3+}$  (iii)  $:\dot{B}$  and  $\left[:\dot{B}$ :  $:\dot{C}:$  (iv)  $:\dot{C}:$  and  $:\dot{C}:$   $:\dot{C}:$ 

(b) (i) 
$$Mg$$
 : or  $[Mg]^{2+}$  [:  $x = 1$ ]  $x = 1$ ]

(ii) 
$$\stackrel{\times}{\text{Al}} \stackrel{\times}{\text{N}} \stackrel{\circ}{\text{N}} = \text{Or} \quad [\text{Al}]^{3+} \left[ \stackrel{\times}{\text{N}} \stackrel{\circ}{\text{N}} \stackrel{\circ}{\text{N}} \right]^{3}$$

(iii) 
$$\overset{\times}{\text{Ca}}$$
 Br. or  $[\text{Ca}]^{2^+}$  2  $[\overset{\times}{\text{Br}}$   $]^-$ 

- 2. (a) NaCl as Na+ ion is smaller in size than Cs+ ion.
  - (b) Stability is dependent on the magnitude of lattice energy. High negative value of lattice energy gives more stability to an ionic compound.
  - (c) MgO and Al<sub>2</sub>O<sub>3</sub> are used as refractory materials because they have high melting points on account of high lattice energies.
- 3. (a) From left to right -1, +1, 0
  - (b) From left to right 0, +1, -1

Thus, structure (b) is preferred as negative charge is present on more electronegative atom.

- 4. (a)  $SF_4$  and  $SF_6$ 
  - (b) (i)  $CH_3I < CH_3Br < CH_3CI < CH_3F$ (ii)  $BF_3 < H_2S < H_2O$
- 5. (a) Ionic Na<sub>2</sub>S, NaH, CaCl<sub>2</sub>, KBr, CaC<sub>2</sub> (However covalent bonding exists between carbon atoms.)

Covalent SnCl<sub>4</sub>, diamond, C<sub>2</sub>H<sub>4</sub>, HCl (gas), NH<sup>+</sup><sub>4</sub>

- (b) (i) Ionic NaCl, (ii) Covalent  $CS_2$ , (iii) Covalent  $SO_2$  and  $SO_3$ , (iv) Ionic  $CaH_2$ .
- (c) (i) Ionic, (ii) Covalent, (iii) Covalent, (iv) Covalent, (v) Ionic, (vi) Covalent, (vii) Covalent and coordinate, (viii) Covalent and coordinate, (ix) Covalent and coordinate, (x) Electrovalent and coordinate. (d) (i) Pure covalent bond, (ii) Semipolar bond, (iii) Electrovalent.
- 6. (i) NaCl is the polar compound as the electronegativity difference is maximum, (ii) NH¼ [NH₃→H]⁺, (iii) HF (electronegativity of fluorine is maximum), (iv) The size of I⁻ ion is larger than F⁻ ion. Hence, more of polarisation by Li⁺ ion in LiI occurs. Thus, LiI is more covalent, (v) p-hydroxybenzaldehyde is more soluble in water as it forms hydrogen bonding with water, (vi) NaCl. Charges are same on the ions but size of Na⁺ ion is smaller than K⁺ and Cs⁺ ions, (vii) CO₂ is a non-polar molecule as it has symmetrical shape, (viii) HF.
- 7. (i) Strength of hydrogen bonding depends on electronegativity of atom linked with hydrogen. Thus, the order is S < Cl < N < O < F (ii) The increasing order is  $F_2 < Cl_2 < O_2 < N_2$ . Both fluorine and chlorine atoms in  $F_2$  and  $Cl_2$  possess three non-bonded electron pairs each. Due to small size of fluorine, there is larger repulsion between non-bonded electrons in comparison to chlorine. Thus,  $F_2$  has lesser dissociation energy than  $Cl_2$ . In oxygen,

two non-bonded electron pairs are present, *i.e.*, less repulsion than  $\text{Cl}_2$  and in nitrogen only one electron pair is present, *i.e.*, minimum repulsion is present. Hence,  $\text{N}_2$  has maximum stability.

(iii)  $NO_2^+ < NO_2^- < NO_3^-$ 

(iv) C-C < C=C < C=C

(Energy increases with multiplicity.)

(v) C≡C < C=C < C-C

(Bond length decreases with multiplicity.)

(vi) Polarity can be decided on electronegativity difference.

$$PH_3 < AsH_3 < SbH_3 < NH_3$$

(viii) BaO < SrO < CaO < MgO

[Hint: Size of cation in decreasing order.]

(ix) 
$$F_2 < O_2^- < O_2 < O_2^+ < N_2$$
  
Bond order 1 1.5 2.0 2.5 3.0  
(x)  $NO^+ < NO < NO^-$ 

Bond order 3 2.5 2

Higher the bond order, smaller is the bond length.

- 8. (i) three; (ii) four; (iii)  $sp^3d$ ,  $sp^3d^2$ ; (iv) three covalent and one coordinate; (v)  $sp^3d$  (bonding pairs + lone pairs = 5); (vi)  $sp^3$  hybridization of oxygen; (vii) linear (both carbon atoms are sp hybridized); (viii) possess stable electronic configuration; (ix) highly electropositive and highly electronegative; (x) covalent; (xi) odd electron; (xii) interhydrogen bonding; (xiii) intrahydrogen bonding; (xiv) two; (xv) bond order—zero; (xvi) diamagnetic.
- 9. (a) If the electronegativity difference is more than 1.7;
  - (b) If the electronegativity difference is less than 1.7;
  - (c) Coordinate bond; (d) (i) covalent, electronegativity difference

10. (i) 
$$O^{+}$$
  $O^{+}$   $O^{+$ 

12. (a)  $sp^3d$ , linear; (b)  $sp^3$ , tetrahedral; (c)  $sp^3d^2$ , square planar; (d)  $sp^3d^2$ , square planar (similar to c); (e) tetrahedral,  $sp^3$ ;

-F; (g) oxygen undergoes sp<sup>3</sup>

hybridization, V-shape structure.

- 13. (a) (i) Fe<sup>3+</sup>
- (iii) Al3+

- (b) (i) I<sup>-</sup>
- (ii) S<sup>2-</sup>
- (iii) N<sup>3-</sup>
- (c) (i) CuS (ii) AgI (iii)  $PbCl_4$  (iv)  $AlCl_3$  (v) LiCl (vi)  $BeCl_2$
- (d) (i) K<sup>+</sup>—F<sup>-</sup> (ii) Na<sup>+</sup>—O<sup>2</sup>-
- (e) (i) NaCl (ii) CaF2 (iii) CaCl2
- 14. (a) (i) Ionic bond with partial covalent character, (ii) covalent, (iii) ionic, (iv) coordinate.
  - (b) (i)  $BF_3$ , (ii)  $BeCl_2$  or  $CO_2$ , (iii)  $BaSO_4$ , (iv)  $CH_4$ ,
  - (v)  $NH_4Cl[(H_3N\rightarrow H)^+Cl^-]$  or  $(H_3N\rightarrow BF_3)$ , (vi) HCl, (vii)  $NH_3$ .
  - (c) (i) NaCl (very small distortion).
  - (ii) MgCl<sub>2</sub> (more ionic than AlCl<sub>3</sub>).
  - (iii) NaCl in molten state (as ions are present in mobile state).
  - (iv)  $NH_{3}$ ,  $(sp^3$  hybridization. One lone pair is present on N-atom).
  - (v) HF (Hydrogen bonding is present. Molecules come nearer to each other and associate through hydrogen bonds).

#### **Answers**: Matching Type Questions

- (A) (a-iv); (b-i); (c-v); (d-ii); (e-iii); (f-vi)
- (B) (1-v-b); (2-vi-d); (3-i-c); (4-ii-f); (5-iii-a); (6-iv-e)
- (C) (a-viii); (b-x); (c-ix); (d-ii); (e-i); (f-vii); (g-iii); (h-v); (i-iv); (j-vi)

# ILLUSTRATIONS OF OBJECTIVE QUESTIONS



- 1. The electronegativity of H and Cl are 2.1 and 3.0 respectively. The correct statement(s) about the nature of HCl is/are:
  - (a) HCl is 17% ionic
- (b) 83% ionic

(c) 50%

(d) 100%

Ans. (a)

[Hint: % ionic character = 
$$16 (X_A - X_B) + 3.5 (X_A - X_B)^2$$
  
=  $16 (3.0 - 2.1) + 3.5 (3.0 - 2.1)^2$   
=  $14.4 + 2.835 = 17.235 \approx 17\%$ ]

- The order of strength of hydrogen bond is:
  - (a) Cl—H....Cl > N—H....N > O—H....O > F—H....F
  - (b) N-H....N > Cl-H....Cl > O-H....O > F-H....F
  - (c) O-H....O > N-H....N > Cl-H....Cl > F-H....F
  - (d) F-H....F > O-H....O > N-H....N > Cl-H....Cl

[Hint: Hydrogen bond strength increases with the increase of electronegativity and decrease in size of the atom.

Electronegativity =  $F > O > N \approx Cl$ 

- The electronegativity of O, F, N, Cl and H are 3.5, 4.0, 3.2, 3.0 and 2.1 respectively. The strongest bond will be:
  - (a) F-O Ans. (d)
- (b) O—Cl
- (c) N—H

[Hint: Bond strength 

difference in electronegativity of atoms.]

- The carbonyl group has following resonating structures:
  - $(I) > \tilde{C} \tilde{O}$
- (II) > C̄—Ō
- (III) > C = O

The correct order of stability of these structures is :

- (a) I > II > III
- (b) III > I > II
- (c) I > III > II
- (d) III > II > I

Ans. (b)

- IHint: The resonating structure with minimum or no charge is more stable. Thus, the stability of (III) form is maximum. The structure (I) is more stable than structure (II) as the negative charge is present on more electronegative atom.]
- Which combination will give the strongest ionic bond?
  - (a) Na<sup>+</sup> and Cl<sup>-</sup>
- (b) Mg<sup>2+</sup> and Cl<sup>-</sup>
- (c)  $Na^+$  and  $O^{2-}$
- (d)  $Mg^{2+}$  and  $O^{2-}$

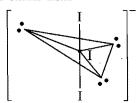
Ans. (d)

[Hint: Ionic bond strength depends on the force of attraction between cation and anion.  $F \propto \frac{q_1 q_2}{r^2}$ 

- 6. Number of bonding pairs and lone pairs around the central atom in the  $I_3^-$  ion are:
  - (a) 2, 2
- (b) 3, 2
- (c) 2, 3
- (d) 4, 3

Ans. (c)

[Hint: There are two bonding pairs and three lone pairs in the outershell of central atom.



- 7. The formal charge on the central oxygen atom in O<sub>3</sub> molecule is:
  - (a) 0

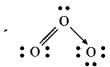
(b) + 1

(c) -1

(d) - 2

Ans. (b)

[Hint: The Lewis dot structure of O3 is:



Formal charge on central oxygen atom = Valence electrons -

½ bonding electrons - non-bonding electrons

$$= 6 - \frac{1}{2} \times 6 - 2 = + 1$$

8. Match List I (species) and List II (bond orders) and select the correct answer:

the correct answer:							
	List I				List II		
A.	$N_2$			1.	1.0		
B.	$O_2$		•	2.	2.0		
C.	$F_2$			3.	2.5		
D.	$O_2^+$			4.	3.0		
	Α	В	C	D			
(a)	4	2	1	3			
(b)	1	3	4	2			
(c)	1	2	4	3			
(d)	4	3	1	2			
Anc	(2)						

**[Hint:**  $N_2 : \sigma(2s)^2 \dot{\sigma}(2s)^2 \pi (2p_x)^2 \pi (2p_y)^2 \sigma (2p_z)^2$ ;

Bond order = 
$$\frac{1}{2}(8-2) = 3$$

 ${\rm O}_2 \,:\, ({\rm G2}s)^2 \,({\rm \mathring{c}2}s)^2 \,({\rm G2}p_z)^2 (\pi_u 2p_u)^2 (\pi_z 2p_x)^2 \,({\rm \mathring{\pi}}_u 2p_u)^1 ({\rm \mathring{\pi}}_z 2p_x)^1;$ 

Bond order = 
$$\frac{1}{2}(8-4) = 2$$

 $F_2: (\sigma 2s)^2 (\mathring{\sigma} 2s)^2 (\sigma 2p_z)^2 (\pi_u 2p_u)^2 (\pi_z 2p_x)^2 (\mathring{\pi}_u 2p_u)^2 (\mathring{\pi}_z 2p_x)^2;$ 

Bond order = 
$$\frac{1}{2}(8-6) = 1$$

 $O_2^+: (\sigma 2s)^2 (\mathring{\sigma} 2s)^2 (\sigma 2p_z)^2 (\pi_y 2p_y)^2 (\pi_z 2p_x)^2 (\mathring{\pi}_y 2p_y)^1;$ 

Bond order = 
$$\frac{1}{2}(8-3) = 2.5$$
]

- 9. Which of the following have identical bond order?
  - (I) CN⁻ (II) O⁻₂ (III) NO⁺ (IV) CN⁺
  - (a) I, III

- (c) II, IV
- (d) I, II, III

Ans. (a)

[Hint: Isoelectronic species have same bond order.

$$CN^- = 6 + 7 + 1 = 14$$
 electrons;  $O_2^- = 8 + 8 + 1$   
= 17 electrons;  $NO^+ = 7 + 8 - 1 = 14$  electrons;  
 $CN^+ = 6 + 7 - 1 = 12$  electrons]

- 10. The ratio of  $\sigma$  to  $\pi$  bonds in mesitylene is :
  - (a) 3

(b) 7

(c) 5

(d) 6

Ans. (b)

[Hint: The structure of mesitylene is:

Total number of σ-bonds Total number of  $\pi$ -bonds = 3

- 11. Both BF<sub>3</sub> and NF<sub>3</sub> are covalent compounds. BF<sub>3</sub> is a nonpolar compound but NF3 is polar. The reason is that:
  - (a) boron is a solid and nitrogen is a gas in free state
  - (b) BF<sub>3</sub> is planar but NF<sub>3</sub> is pyramidal in shape
  - (c) boron is a metalloid while nitrogen is a non-metal
  - (d) atomic size of boron is smaller than that of nitrogen

[Hint: BF3 is planar, hence the dipole moment of the molecule is zero. NF3 is pyramidal, thus it possesses dipole moment. Hence, NF<sub>3</sub> is a polar compound.]

- 12. Which of the following sets of species does not follow octet rule?
  - (a) CO,  $PCl_5$ ,  $PCl_3$ ,  $AICl_3$  (b) CO,  $B_2H_6$ ,  $NH_3$ ,  $H_2O$
  - (c) AlCl<sub>3</sub>, BF<sub>3</sub>, PCl<sub>5</sub>, SF<sub>6</sub>
- (d) H<sub>2</sub>O, NH<sub>3</sub>, CO<sub>2</sub>, AlCl<sub>3</sub>

[Hint: BF<sub>3</sub>, AlCl<sub>3</sub> are electron deficient molecules while in PCl<sub>5</sub> and SF<sub>6</sub> molecules P and S possess more than 8 electrons in their valence shells.]

- 13. Which of the following species is diamagnetic in nature? [A.I.E.E.E. 2005]
  - (a) He<sub>2</sub><sup>+</sup>

Ans. (c)

(b) H<sub>2</sub>

(c)  $H_2^+$ 

(d) H<sub>2</sub>

Ans. (b)

Ans. (b)

[Hint:  $He_2^+$ :  $(\sigma 1s)^2 (\sigma 1s)^1$  one unpaired electron – paramagnetic

 $H_2: (\sigma 1s)^2$  no unpaired electron - diamagnetic

 $H_2^+$ :  $(\sigma 1s)^1$  one unpaired electron - paramagnetic

 $H_2^-: (\sigma 1s)^2 (\mathring{\sigma} 1s)^1$  one unpaired electron - paramagnetic]

- 14. The number and type of bonds between two carbon atoms in calcium carbide are: [A.I.E.E.E. 2005]
  - (a) one sigma, one pi
- (b) one sigma, two pi
- (c) two sigma, one pi
- (d) two sigma, two pi

[Hint: Calcium carbide is an ionic compound having anion [:C=C:]<sup>2-</sup>. It has one sigma and two pi bonds.]

15. [In Ag (CN)<sub>2</sub>], the number of  $\pi$ -bonds is :

[A.I.J.M.S. 2006]

(a) 2

(b) 3

(c) 4

(d) 6

Ans. (c)

[Hint: The cyanide ion consists a triple bond, —C=N-, i.e., one sigma and two  $\pi$ -bonds are present: thus, two cyanide groups have  $4\pi$ -bonds.]

- 16. Which of the following molecules/ions does not contain unpaired electrons? [A.I.E.E.E. 2006]
  - (a)  $O_2^{2-}$

(b) B<sub>2</sub>

(c)  $N_2^+$ Ans. (a) (d) O<sub>2</sub>

17. In which of the following molecules/ions are all the bonds [A.I.E.E.E. 2006] not equal?

(a) SF<sub>4</sub>

(b) SiF<sub>4</sub>

(c) XeF<sub>4</sub>

(d) BF<sub>4</sub>

Ans. (a)

[Hint: In  $SF_4$ , sulphur undergoes  $sp^3d$  hybridization. It contains two axial and two equatorial bonds and one position is occupied by a lone pair of electrons.]

- 18. H<sub>2</sub>, Li<sub>2</sub>, B<sub>2</sub> each has bond order equal to 1, the order of their stability is:
  - (a)  $H_2 = Li_2 = B_2$
- (c)  $H_2 > B_2 > Li_2$
- (b)  $H_2 > Li_2 > B_2$ (d)  $B_2 > Li_2 < H_2$

Ans. (c)

[Hint: H2, Li2, B2 are not equally stable. Li atom is much larger in size than H-atom. The bond length in Li2 is much larger than bond length in H2. Moreover, Li2 molecule has two electrons in the antibonding molecular orbital while  $H_2$  has no electrons in the antibonding molecular orbital. Thus, Li<sub>2</sub> is less stable than H<sub>2</sub> (Bond energy of Li<sub>2</sub> = 110 kJ  $\text{mol}^{-1}$  + Bond energy of  $H_2 = 438 \text{ kJ mol}^{-1}$ ). Boron atom is smaller than lithium atom but larger than hydrogen atom. The B2 is more stable than Li2 but less stable than  $H_2$  (Bond energy of  $B_2 = 290$  kJ mol<sup>-1</sup>).]

- 19. Which of the following pair is expected to have the same bond order?
  - (a)  $O_2$ ,  $N_2$
- (b)  $O_2^+$ ,  $N_2^-$
- (c) O<sub>2</sub>, N<sub>2</sub><sup>+</sup>
- (d)  $O_2$ ,  $N_2$

**[Hint:**  $O_2^+$ ,  $N_2^-$  — Each has 15 electrons. Bond order =  $\frac{1}{2}$  (10 – 5)

- 20. Pick out the incorrect statement:
  - (a) In PCl<sub>5</sub>, P atom is sp<sup>3</sup>d hybridized and has trigonal bipyramidal geometry
  - (b) PCl<sub>5</sub> on hydrolysis forms oxychloride
  - (c) PCl5 acts as a Lewis acid
  - (d) In PCl<sub>5</sub>, the axial chlorine atoms are closer to central P atom than equatorial chlorine atoms

Ans. (d)

# **OBJECTIVE QUESTIONS**



## Set I: This set contains questions with single correct answer.

1.	When two atoms combine to form a molecule:			(a) S and Q	□ (b) P and I	₹ /	
	(a) energy is released			(c) S and R	☐ (d) S and I	•	
	(b) energy is absorbed			[Hint: As Q is chlorine	and S is potass	ium, so they i	form
	(c) energy is neither released nor absorbed			KCl which is an		•	
	(d) energy may either released or absorbed		11.	The electronic configurat	_		
2.	Valency expresses:			$A: 1s^2, 2s^2 2p^6, 3s^2 3p^4$		$2p^6$ , $3s^2$ $3p^5$	
	(a) total electrons in an atom			$C: 1s^2, 2s^2 sp^6, 3s^1$	$D: 1s^2, 2s^2$	$2n^6 \cdot 3s^2$	
	(b) atomicity of an element			The formulae of ionic c		•	med
	(c) oxidation number of an element			between them are:	ompounds mur	COULT DC 101	
	(d) combining capacity of an element			(a) $A_2C$ , $DA$ , $CB$ , $D_2B$	☐ (b) C <sub>2</sub> A, D	A CR DR	
3	Electronic theory of valency was presented by:	L-J		(c) AC, D <sub>2</sub> A, C <sub>2</sub> B, DB	$\square  \text{(d) } C_2A, D$		
o.	(a) Pauling		12.	Among sodium phospha			
	(c) Kossel and Lewis		12.	chloride the solubility in			******
4		ш		(a) sulphate > phosphate			
4.	The combination of atoms occur because they want:	1.11		(b) chloride > sulphate >			
	(a) to decrease number of electrons in the outermost or			(c) chloride > phosphate			
				(d) phosphate > chloride	_	•	
	(b) to attain an inert gas configuration		`	[Hint: For the same cati	-	ituda of chara	
	(c) to increase number of electrons in the outermost or			the anion increase	_	-	
•				thus, solubility v		rgies increase	anu
	(d) to attain 18 electrons in the outermost orbit		13	Lattice energy of an ionic		ande on :	
5.	An electrovalent bond is formed between:		15.	Lattice energy of all follow	c compound de	[A.I.E.E.E. 2	70057
	(a) two electronegative atoms			(a) charge on the ion on	1,,	[CArlelia Lielia A	
	(b) two metals			(b) size of the ion only	ıy		
	(c) electropositive and electronegative atoms			(c) packing of the ion of	2122	,	
	(d) two electropositive atoms						
6.	Most favourable conditions for electrovalent bonding a	are:	14	(d) charge and size of th In covalency:	e ion		L
	[D.P.M.T. 20	05]	14.	•	taleas mlasa		
	(a) low ionisation potential of one atom and high electronic	ron		<ul><li>(a) transfer of electrons</li><li>(b) one atom acts as don</li></ul>	-	ka an daaantaw	
	affinity of the other atom					-	
	(b) high electron affinity and high ionisation potential	of	1	(c) the electrons are sharing of old			
	both the atoms			(d) equal sharing of ele atoms	ections takes p	ace between	
	(c) low electron affinity and low ionisation potential	of	15	A covalent bond is poss	ible between		ш
	both the atoms		13.	(a) similar atoms	ible between.		
	(d) high ionisation potential of one atom and low electrons	ron		(b) dissimilar atoms		•	
	affinity of the other atom		1	(c) similar and dissimilar	r atome	**	´ 🗖
7.	The crystal lattice of electrovalent compound is compound	sed		(d) similar molecules	n atoms		
	of:		16	Multiple covalent bonds	eviet in a mole	cula of	11
	(a) atoms   (b) molecules		10.	(a) $F_2$	☐ (b) N <sub>2</sub>	cuic oi.	
	(c) oppositely charged ions			(a) F <sub>2</sub> (c) CH <sub>4</sub>	$\Box  (d) \ H_2$		
	(d) both molecules and ions		17.	Which of the following st		rue about cov	
8.	The electronegativity of cesium is 0.7 and that of fluor		17.	compounds?	atements is not	rue about cov	aicin
	is 4.0. The bond formed between the two is:			(a) They may exhibit sp	aca isomorism		
	(a) covalent			(b) They have low melti		nainta	
	(c) coordinate			(c) They show ionic rea		pontis	
9.	Electrovalent bond is formed by:	Tanal		(d) They show notice rea			
٠.	(a) sharing of electrons □ (b) donation of electrons	П	1Ω			and V is stee	
	(c) transfer of electrons $\Box$ (d) none of these		10.	Element <i>X</i> is strongly electronegative. Both are	_		
0.	Four elements $P$ , $Q$ , $R$ , $S$ have atomic numbers $Z-1$ ;			would be:	and variety, THE	compound for	. ILIÇU
٠.			t d	(a) X <sup>+</sup> Y <sup>-</sup>	□ (b) <i>X</i> — <i>Y</i>		
	Z + 1 and $Z + 2$ respectively. If $Z$ is 17, then bond between which pair of elements will be most ionic?	een	1	(c) X <sup>-</sup> Y <sup>+</sup>	$\square  \text{(d) } X \rightarrow Y$		
	WINCH DAIF OF EICHICHUS WIFE DE MOST TORIC !		1	(w) 21 I	$ (u) \Lambda - 1$		

19.	In a triple bond there is sharing of :	32.	A molecule possessing dipole moment is:	
	(a) 3 electrons $\Box$ (b) 4 electrons $\Box$	:	(a) $CH_4$	
	(c) several electrons $\Box$ (d) 6 electrons $\Box$		(c) $BF_3$ $\square$ (d) $CO_2$	
20.	Element A has 3 electrons in the outermost orbit and	33.	In which of the following molecules the bond angle	is
	element B has 6 electrons in the outermost orbit. The		maximum?	
	formula of the compound formed between A and B would		(a) $CH_4$ $\Box$ (b) $H_2O$	
	be:		(c) $NH_3$ $\square$ (d) $CO_2$	
	(a) $A_2B_3$ $\Box$ (b) $A_2B_6$ $\Box$		CO <sub>2</sub> is isostructural with:	
	(c) $A_2B$ $\Box$ (d) $A_3B_2$ $\Box$	0	(a) $SO_2$ $\square$ (b) $HgCl_2$	
21	The formula of the compound is $A_2B_5$ . The number of		(c) $C_2H_2$ $\square$ (d) $SnCl_2$	
<b>4</b> 1,	electrons in the outermost orbits of A and B respectively	25	Both ionic and covalent bonds are present in:	
		30.		П
	are:		•	
	(a) 6 and 3	26	(c) KC1	
	(c) 5 and 2	36.	The compound with the highest boiling point is:	_
22.	Which shows the highest lattice energy?		(a) CH <sub>3</sub> OH □ (b) CH <sub>3</sub> Br	
	(a) RbF		(c) $CH_3Cl$	
	(c) NaF	37.	The bond between carbon atom (1) and carbon atom (2)	in
23.	Polarisation is the distortion of the shape of an anion by		compound,	
	the cation. Which of the following statements is correct?		$N=C-CH=CH_2$ involves the hybrid as:	
	(a) Maximum polarisation is done by a cation of high		(1) (2)	
	charge		(a) $sp$ and $sp^2$ $\square$ (b) $sp^2$ and $sp^3$	
	(b) A large cation is likely to bring large degree of		(c) $sp$ and $sp^3$ $\square$ (d) $sp$ and $sp$	
	polarisation $\square$	38.	The bonds present in N <sub>2</sub> O <sub>5</sub> are:	
	(c) A smaller anion is likely to undergo a high degree of		(a) only ionic	
	polarisation		(b) covalent and coordinate	
	(d) Minimum polarisation is done by a cation of small size		(c) only covalent   (d) covalent and ionic	
		39.	The hydrogen bond is strongest in: [A.I.E.E.E. 20]	07]
24.	Variable valency is shown by:		(a) O—H S	
	(a) s-block elements $\Box$ (b) d-block elements $\Box$		(c) F—H F	
	(c) $p$ - and $d$ -block elements	40.	The sigma and $\pi$ -bonds present in benzene ring are:	
	(d) all elements		(a) three sigma three pi	
25.	The most covalent halide is:		(b) six sigma and three pi	
	(a) $AlF_3$ $\Box$ (b) $AlCl_3$ $\Box$		(c) six pi and three sigma	
	(c) $AlBr_3$ $\Box$ (d) $AlI_3$ $\Box$		(d) nine sigma and three pi	
26.	A $\pi$ -bond is formed by the overlap of :	41.	Hydrogen bonding is maximum in:	
	(a) $s$ - $s$ orbitals $\Box$ (b) $s$ - $p$ orbitals $\Box$		(a) ethanol	
	(c) $p$ - $p$ orbitals in end to end fashion		(c) ethyl chloride	
	(d) <i>p-p</i> orbitals in sidewise manner	42.		
27.	In the formation of ethylene molecule, the carbon atom		(a) $sp$ $\Box$ (b) $sp^2$	
-	makes use of:	,	(c) $sp^3$ $\Box$ (d) $dsp^2$	
	(a) $sp^3$ hybridization $\Box$ (b) $sp^2$ hybridization $\Box$	43.	Molecule in which the distance between two adjacent carl	on
	(c) $sp$ hybridization $\square$ (d) none of these $\square$		atoms is largest, is:	
28.	Which of the following has a giant covalent structure?		(a) benzene	
	(a) $CCl_4$ $\Box$ (b) $SiO_2$ $\Box$		(c) ethene $\Box$ (d) ethane	
	(c) $SiCl_4$ $\square$ (d) $CO_2$ $\square$	44.	Which of the following compounds of IV group eleme	ents
29.			would you expect to be most ionic in character?	
	(a) $NH_3$ $\square$ (b) $SiF_4$ $\square$			
	(c) $H_2O$ $\square$ (d) $BF_3$ $\square$		(c) $PbCl_2$ $\square$ (d) $PbCl_4$	
30.		45.	The octet rule is not valid for the molecule:	
	overlapping?		(a) CO <sub>2</sub>	
	(a) $Cl_2$		(c) $O_2$ $\square$ (d) $CO$	
	(c) $H_2O$ $\square$ (d) $NH_3$ $\square$	46.	The compound which contains both ionic and coval	
31.	104.5° is the bond angle present in:	-0.	bonds is:	
- 4.	(a) H <sub>2</sub> O		(a) CH <sub>4</sub>	
	(a) NH		(a) VCN	

<b>47</b> .	The type of bonds present in CuSO <sub>4</sub> ·5H <sub>2</sub> O are:		60.	Which is the weakest am	ong the following types of bon	ds?
	(a) electrovalent, covalent and coordinate			(a) Ionic bond	☐ (b) Covalent bond	
	(b) electrovalent and covalent			(c) Metallic bond	☐ (d) Hydrogen bond	
	(c) electrovalent and coordinate		61.	In a series ethane, ethyle	ne and acetylene, the C—H bo	ond
	(d) covalent and coordinate			energy is:	•	
48.	The ion that is isoelectronic with CO is:			(a) the same in all the th	rree compounds	
	(a) $CN^-$			(b) greatest in acetylene	•	
	(c) $O_2^-$			(c) greatest in ethylene		
49.	The types of bonds present in NH <sub>4</sub> Cl are:			(d) greatest in ethane	•	
	(a) electrovalent, covalent and coordinate		62.	The high boiling point o	f water is due to:	
	(b) only ionic			(a) its high specific heat		
	(c) only covalent			(b) hydrogen bonding b		
	(d) covalent and coordinate			(c) weak dissociation of		
50.	On hybridization of one s- and one p-orbitals, we get:			(d) its high dielectric con		
	(a) two mutually perpendicular orbitals		63.		onds formed by axial overlap o	
	(b) two orbitals at 180°		"		ll of participating atoms decrea	
	(c) four orbitals directed tetrahedrally			as:	a or paracipaning atomo access	
	(d) three orbitals in the plane				□ (b) $s$ – $s$ > $p$ – $p$ > $s$ – $p$	
51	If a molecule $MX_3$ has zero dipole moment, the significant			(c) $p-s > s-s > p-p$		
J1.	bonding orbitals used by $M$ are:	511,121			aximum axial overlap and s-orb	
	(a) pure $p$ $\square$ (b) $sp$ hybrids			have minimum.]	laximum axiai overiap and 3-010	Itais
	(c) $sp^2$ hybrids / $\Box$ (d) $sp^3$ hybrids		64	The triple bond in ethyn	e is made of	
52.	The species in which the central atom uses $sp^2$ hybrid		01.	(a) three sigma bonds	ic io italia or	
32.	its bonding is:	5 III		(b) three $\pi$ -bonds		
				(c) one sigma and two 1	<del>I</del> -honds	
	(a) PH <sub>3</sub> □ (b) AsH <sub>3</sub> (c) NH <sub>3</sub> □ (d) CH <sub>3</sub> +			(d) two sigma and one a		
52		ш	65	The linear structure is as		
53.	The molecule that has linear structure is:		00.		B: NCO	
	(a) CO <sub>2</sub>			$A : SnCl_2$ $C : NO_2^+$	D: CS <sub>2</sub>	
E 4	(c) $SO_2$				$\square \text{ (b) B, C and D}$	
<b>54</b> .	The Cl—C—Cl angle is 1, 1, 2, 2-tetrachloroethene	and		(a) A, B and C		
	tetrachloromethane respectively will be about:	_	- 66	(c) A, C and D	(d) none	u
	(a) 109.5° and 90°		00.	Which of the following		r1
	(c) 90° and 109.5°			(a) $O_2^+$	$\square  \text{(b) } O_2$	
55.	· ·	1	67	(c) $O_2^-$	(d) O <sub>2</sub> <sup>2</sup>	ш
	(a) by transfer of one electron from one atom to anot		67.	Acetylene molecule con		
	AND deal for detailed had detailed			(a) 5 sigma bonds		
	(b) by the loss of one electron each from both the atoms		60		Is $\Box$ (d) 2 sigma and $3\pi$ -bond	s ப
	(c) by sharing of one electron from each atom		00.		ring has a coordinate bond?	_
	(d) when contribution of one electron pair is made by			(a) NaCl	□ (b) Cl <sub>2</sub>	
<b>-</b> /	atom and both the atoms share equally		60	(c) NH <sub>4</sub> Cl	(d) AlCl <sub>3</sub>	
56.	The molecule which has highest dipole moment amo	ngst	09.		bonds in 1-butene-3-yne are:	_
	the following is:			(a) 5 sigma and 5 pi	☐ (b) 7 sigma and 3 pi	
	(a) CH <sub>4</sub>		70	(c) 8 sigma and 2 pi	☐ (d) 6 sigma and 4 pi	
	(c) CCl <sub>4</sub>		70.	Which of the following		-
57.	·			(a) $O_2^-$	□ (b) CN <sup>-</sup>	
	(a) zero			(c) CO	☐ (d) NO <sup>+</sup>	
	(c) 2		71.	Which molecule has zer	-	,
58.				(a) CH <sub>2</sub> Cl <sub>2</sub>	☐ (b) BF <sub>3</sub>	
	(a) one		-	(c) NF <sub>3</sub>	$\square  (d)  ClO_2$	
	(c) between one and two		72.		th $CO_2$ and $N_3$ , which one is	the
	(d) one and two, alternately			structure of N <sub>2</sub> O?		
59.	Which of the following would have a permanent di	pole		(a) N—O—N	□ (b) N≡N→O	
	moment?	·		()	+	
	(a) $SiF_4$ $\Box$ (b) $SF_4$			(c) $N$	□ (d) N O	
	(c) $XeF_4$			14	0	

73.	Number of bonds in benzene: [D.P.M.T. 2005]		(a) $dsp^3$ hybridisation $\square$ (b) $d^2sp^3$ hybridisation $\square$
	(a) $6 \sigma$ and $3 \pi$		(c) $dsp^2$ hybridisation $\Box$ (d) $sp^3d$ hybridisation $\Box$
	(c) $12 \sigma$ and $3 \pi$ $\square$ (d) $6 \sigma$ and $6 \pi$ $\square$	86	6. Which among the following compounds does not show
74.	The shape of sulphate ion is:		hydrogen bonding?
	(a) hexagonal		(a) Phenol
	(c) trigonal bipyramidal (d) tetrahedral	ı	(c) Acetic acid □ (d) Diethyl ether □
75.	Structure of ammonia is:	87	7. How many resonating forms can be written for nitrate and
	(a) pyramidal		chlorate ions respectively?
	(c) trigonal	ı İ .	(a) 3, 2
76.	Oxygen molecule is paramagnetic because:		(c) 2, 3
	(a) bonding electrons are less than antibonding electrons		
			[Hint: $0 - \dot{N} = N$
	(b) bonding electrons are more than antibonding electrons	;	0 0
		]	
	(c) it contains unpaired electrons	1.	0"   `0
	(d) bonding electrons are equal to antibonding electrons	88	B. A molecule may be represented by three structures having
		ון וי	energies $E_1$ , $E_2$ and $E_3$ respectively. The energies follow the
<i>7</i> 7.	Resonance structure of a molecule should not have:		order $E_3 < E_2 < E_1$ . If the actual energy content of the
	(a) identical arrangements of atoms	]	molecule is $E_0$ , the resonance energy is :
	(b) nearly same energy content	]	(a) $(E_1 + E_2 + E_3) - E_0$
	(c) the same number of paired electrons	1	(a) $(E_1 + E_2 + E_3) - E_0$
	(d) identical bonding	]   80	9. On the basis of resonating structures of $CO_3^{2-}$ ion, the
78.	The bond order of a molecule is given by:	0;	C—O bond order is:
	(a) total number of electrons in bonding and antibonding	3	(a) 1.5
	orbitals	]	(c) 1.33
	(b) the difference between the number of electrons in	1   90	0. Which carbon atom is most electronegative?
	bonding and antibonding orbitals	]   ^	(a) Unhybridised carbon $\square$ (b) $sp$ hybridised carbon $\square$
	(c) twice the difference between the number of electron	s	(c) $sp^2$ hybridised carbon $\square$ (d) $sp^3$ hybridised carbon $\square$
	in bonding and antibonding orbitals	l l	[Hint: Higher s-character in hybridization brings more electro-
•	(d) half the difference between the number of electrons in		negativity.]
	bonding and antibonding orbitals	]   '9	1. The maximum possible number of hydrogen bonds in
79.			which a water molecule can participate is:
	(a) ICl (b) BCl <sub>3</sub>		[C.E.T. (Karnataka) 2008]
	(c) $NH_3$ $\square$ (d) $PCl_3$	J	(a) 1
80.	A sp <sup>3</sup> hybrid orbital contains:	.	(c) 3
	(a) 1/4 s-character	1 2.	2. Which of the following statements is true about
01	(c) 2/3 s-character	J	$[Cu(NH_3)_4]SO_4$ ?
81.	Identify the incorrect statement:	<b>,</b> !	(a) It has coordinate as well as covalent bonds
	(a) There are two $\pi$ and one sigma bonds in N <sub>2</sub> .		(b) It has only coordinate bonds
	(b) The hybridisation of oxygen in $H_2O$ is $sp^3$ .	l l	<ul><li>(c) It has only electrovalent bonds</li><li>□</li><li>(d) It has electrovalent, covalent as well as coordinate bonds</li></ul>
	(c) Solid NaCl is a bad conductor of electricity.  (d) Hydrogen bond is a chemical bond.		
92	, 8		3. Which of the following is not a linear molecule?
82.	Metallic lustre is explained by : [D.C.E. 2005 (a) oscillations of loose electrons	_	(a) $CO_2$ $\Box$ (b) $C_2H_2$ $\Box$
	(b) diffusion of metal ions	- 1	(c) HCN $\square$ (d) $H_2O$ $\square$
	(c) excitation of free protons	- 1	4. The bond angles of NH <sub>3</sub> , NH <sub>4</sub> and NH <sub>2</sub> are in the order:
	(d) existence of bcc lattice	1 '	(a) $NH_2^- > NH_3 > NH_4^+ \square$ (b) $NH_4^+ > NH_3 > NH_2^- \square$
83.	A molecule, which contains unpaired electrons is:	<b>-</b>	(c) $NH_3 > NH_2 > NH_4 \square$ (d) $NH_3 > NH_4 > NH_2 \square$
00.	(a) $CO_2$ $\Box$ (b) $N_2$	9 ا ٦	5. As compared to covalent compounds, electrovalent com-
	<del>-</del>	<u> </u>	pounds generally have:
٠.	1	_	(a) low melting points and low boiling points
84.	Which has the bond order $\frac{1}{2}$ ?		(b) low melting points and high boiling points □
	(a) $O_2$ $\square$ (b) $N_2$	□	(c) high melting points and low boiling points
	(c) $F_2$ $\square$ (d) $H_2^+$	_   ~	(d) high melting points and high boiling points
85.	The maximum number of 90° angles between bond pair	-   9	26. Coordinate covalent bond is formed by:
	bond pair of electrons is observed between:		(a) transfer of electrons  (b) sharing of electrons  (c) denotion of electrons  (d) none of these
	[A.I.E.E.E. 2004	IJ	(c) donation of electrons $\square$ (d) none of these $\square$

97.	The molecule which does not exhibit dipole moment is:		(a) (i) and (ii)	☐ (b) (i) and (iv)	
	(a) $NH_3$	1	(c) (i) and (iii)	☐ (d) (ii), (iii) and (iv)	
	(c) $H_2O$	111.	Which one of the follow	wing molecule is trigonal bi	pyra-
	, ^ ^ /		midal?		
			(a) $BF_3$	□ (b) CH <sub>4</sub>	
98.	How many bonds are there in ?		(c) PCl <sub>5</sub>	$\square$ (d) SF <sub>6</sub>	
		1		formed due to the follo	wing
	[D.C.E. 2005]		hybridized orbitals:	3	
	(a) $14  \sigma, 8  \pi$	1	(a) $dsp^2$	$\Box  \text{(b) } sp^3$	
	(c) $14 \sigma$ , $2\pi$		(c) $sp^3d$	•	. 🗆
99.	Hybridisation of the atom changes in :	113.		of four elements a, b, c and c	
	(a) $\underline{\mathbf{AlH}}_3$ to $\underline{\mathbf{AlH}}_4$ $\Box$ (b) $\underline{\mathbf{H}}_2\underline{\mathbf{O}}$ to $\underline{\mathbf{H}}_3\underline{\mathbf{O}}^+$		(i) $1s^2$ (ii) $1s^2$ , $2s^2$ $2p^2$ (	iii) $1s^2$ , $2s^2 2p^5$ (iv) $1s^2$ , $2s^2 2p^5$	o°
100	(c) $\underline{N}H_3$ to $NH_4^+$ $\square$ (d) all of these $\square$		The tendency to form e	lectrovalent bond is greatest	in:
100.	In which of the following the central atom does not use sp		(a) (i)	□ (b) (ii)	
	hybrid orbitals in its bonding?		(c) (iii)	□ (d) (iv)	
	(a) $BeF_3$ $\square$ (b) $OH_3^+$ $\square$ (c) $NH_2^ \square$ (d) $NF_3$ $\square$	114	. Hydrogen bonding is n	naximum in:	
101			(a) ethanol	☐ (b) diethyl ether	
101.	The hybridization of carbon atoms in C—C single bond o	1	(c) ethyl chloride	(d) triethylamine	
	$HC = C - CH = CH_2$ is:	115	. The central atom assum	nes sp <sup>3</sup> hybridization in:	_
. *	(a) $sp^3 - sp^3$ $\square$ (b) $sp^2 - sp^3$ $\square$ (c) $sp - sp^2$ $\square$ (d) $sp^3 - sp$ $\square$		(a) PCl <sub>3</sub>	□ (b) SO <sub>3</sub>	-
100	The type of hybrid orbitals used by the chlorine atom in		(c) BF <sub>3</sub>	$\square$ (d) NO $\frac{1}{3}$	
102.	ClO <sub>2</sub> is:	116		dduct readily because they for	orm:
	(a) $sp^3$			☐ (b) a covalent bond	
	(c) $sp$ $\square$ (d) none of these $\square$			☐ (d) a coordinate bond	
103	Amongst LiCl, BeCl <sub>2</sub> , MgCl <sub>2</sub> and RbCl the compounds with	11/	_	r boiling point than PH <sub>3</sub> beca	
100.	greatest and least ionic character, respectively are:		(a) ammonia has larger		
	(a) LiCl and RbCl $\Box$ (b) RbCl and BeCl <sub>2</sub> $\Box$		(b) ammonia undergoes	and the second s	
	(c) RbCl and MgCl <sub>2</sub> $\square$ (d) MgCl <sub>2</sub> and BeCl <sub>2</sub> $\square$			onic bonds whereas PH <sub>3</sub> cor	
104.	BeF <sub>2</sub> has zero dipole moment whereas H <sub>2</sub> O has a dipole	1	covalent bond	•	
	moment because:	1	(d) ammonia form hydr	_	🗆
	(a) water is linear	118		observed bond lengths of	
	(b) H <sub>2</sub> O is bent	l l		tly the same and the leng	
	(c) F is more electronegative than O		is because of:	single and double bond leng	zın. 11
	(d) hydrogen bonding is present in H <sub>2</sub> O		(a) hybridization	☐ (b) resonance	
105.	Which of the following geometrical configuration	i.	(c) coordinate bonding	and the second s	
	correspond to dsp <sup>2</sup> hybridization?	119	The molecule which has		
	(a) Tetrahedral	117	(a) $SO_3$	□ (b) PCl <sub>3</sub>	
	(c) Square planar		(c) CO <sub>3</sub> <sup>2</sup>	$\square  (d) \ NO_3^-$	
106.	Which one of the following bonds has the highest average	120		h C uses its $sp^3$ hybrid orbita	
	bond energy?		bond formation is:		
	(a) $S=O$ $\square$ (b) $C=C$	1	(a) HČOOH	☐ (b) (H <sub>2</sub> N) <sub>2</sub> CO	
	(c) $C = N$ $\square$ (d) $N = N$	1	(c) (CH <sub>3</sub> ) <sub>3</sub> ČH	☐ (d) CH <sub>3</sub> CHO	
107.	Which one of the following is not paramagnetic?	121		nion favour least covalent char	
	(a) $O_2$ $\square$ (b) $O_2^{\overline{2}}$ $\square$	1	(a) Small, large	☐ (b) Large, small	
	(c) $O_2^+$		(c) Large, large	☐ (d) Small, small	
108.	Which of the following has a tetrahedral structure?		. T-type shape is exhibite	ed by the molecule:	
	(a) $NH_3$		(a) ClF <sub>3</sub>	☐ (b) CHCl <sub>3</sub>	
	(c) $NH_4^+$		(c) CCl <sub>4</sub>	☐ (d) PCl <sub>5</sub>	. $\square$
109.	Among the following ions which one has the highest	123	<del>_</del>	e having a three centre bond	_
	paramagnetism?	,	(a) BN (c) NaBH <sub>4</sub>	$\Box  \text{(b) } H_3BO_3$ $\Box  \text{(d) } B_2H_6$	
	(a) $[Cr(H_2O)_6]^{3+}$	124		molecule with 25% s-charact	
					***
110	(c) $[Cu(H_2O)_6]^{2+}$	]		The state of the s	
110	(c) $[Cu(H_2O)_6]^{2^+}$ $\Box$ (d) $[Zn(H_2O)_6]$ $\Box$ Pick out the isoelectronic structures from the following? (i) $CH_3^+$ (ii) $H_3O^+$ (iii) $NH_3$ (iv) $CH_3^-$	1	hybrid orbital is: (a) plane triangular	☐ (b) linear	□.

-	. 2. 2		•				
125.	Knowing that $Na^+ > Mg^{2+}$ and $S^{2-} > Cl^-$ , predict whi	ch		(c) square planar			
	compound will be least soluble in polar solvent?	1		(d) distorted trigonal bip			
	(a) MgS	□	136.	The shape of ClO3 accord	ing to VSEPR mo	odel is:	
	(c) MgCl <sub>2</sub>			(a) planar triangle	□ (b) pyramid	al ·	
126.	Which of the following elements shows the capacity to for	m		(c) tetrahedral	☐ (d) square p	lanar	
	hybrid orbitals by using s,p and d-atomic orbitals?		137.	The correct order of incre			CO,
•				$CO_{3}^{2-}$ $CO_{2}$ is:		9; C.B.S.E. 20	
				(a) $CO_3^{2-} < CO_2 < CO$			
127.		in		(c) $CO < CO_3^{2-} < CO_2$			
	tetrahedral structure is:			The geometry of H <sub>2</sub> S and		_	_
	(a) NH <sub>3</sub>			(a) angular and non-zero	-	ent are.	
	<del>-</del>			<del>-</del>			
120				(b) angular and zero			
120.	The correct order of the O—O bond length in $O_2$ , $H_2O_2$ at	na		(c) linear and non-zero	,		
	$O_3$ is:	_		(d) linear and zero	701 1 7 1		
	(a) $O_3 > H_2O_2 > O_2$	□	139.	In the compounds of type			the
	(c) $O_2 > O_3 > H_2O_2$			angles Cl—E—Cl for diffe			
	[Hint: Bond between —O—O— in H <sub>2</sub> O <sub>2</sub> is a single bo	1			$\Box  \text{(b) } B > P > A$		
	[1.48 Å]. Bond between O—O in O <sub>3</sub> is intermedia			(c) $B < P = As = Bi$	· ·		
	between single and double bonds due to resonar	1	140.	The formal charges on	three oxygen	atoms of oz	zone
	(1.278 Å) while bond between O2 molecule is	a		molecule are respectively	<b>'</b> :		
	double bond (1.21 Å).]				□ (b) 0, 0, 0		
129.	BCl <sub>3</sub> is a planar molecule whereas NCl <sub>3</sub> is pyramic	lal		(c) +1, 0, -1	□ (d) -1, +1, -	1	
	because:	_	141.	In the compound $\overset{1}{\text{CH}_2}$	=CH $-$ CH $-$ CH	<sub>12</sub> —Č≕ČH,	the
	(a) nitrogen atom is smaller than boron atom			2 3		- T	
	(b) BCl <sub>3</sub> has no lone pair of electrons whereas NCl <sub>3</sub> has			C—C bond is of the type	:: 		_
	lone pair of electrons			(a) $sp - sp^2$	$\Box$ (b) $sp^3 - sp^3$		
	(c) N—Cl bond is more covalent than B—Cl bond		140				
	(d) B—Cl bond is more polar than N—Cl bond		142.	In XeF <sub>2</sub> , XeF <sub>4</sub> and XeF <sub>6</sub> t			
130.	Which of the following molecules is planar?			respectively:		[A.I.E.E.E. 2	
	(a) $XeF_4$ $\Box$ (b) $NF_3$			(a) 2, 3, 1	□ (b) 1, 2, 3		
	(c) $SiF_4$			(c) 4, 1, 2	$\Box$ (d) 3, 2, 1		
131.	Which one is the correct statement with reference	to	143.	Number of sigma bonds	a contract of the contract of	[A.I.E.E.E. 2	002]
	solubility of MgSO <sub>4</sub> in water?			(a) 6	□ (b) 7		
	(a) Hydration energy of MgSO <sub>4</sub> is higher in comparison	to		(c) 17	□ (d) 16	•	
	its lattice energy		144.	Which of the following of	loes not contain o	coordinate bo	ond?
	(b) Ionic potential of Mg <sup>2+</sup> is very low				{P.	M.T. (Raj.) 2	002]
	(c) $SO_4^{2-}$ ion mainly contributes towards hydration ener	gy		(a) $BH_{\frac{4}{2}}$	$\Box$ (b) NH <sub>2</sub>		
				(c) $CO_3^{2-}$	☐ (d) H <sub>3</sub> O	**	
	(d) Sizes of Mg <sup>2+</sup> and SO <sub>4</sub> <sup>2-</sup> are similar		145.	Which of the following h	as $p\pi$ - $d\pi$ bonding	? [C.B.S.E. 2	2002]
132.	Which of the following compounds has a 3 centre bond	?		(a) $NO_3^-$	$\Box$ (b) SO <sub>3</sub> <sup>2-</sup>		
	(a) $BF_3$ $\Box$ (b) $NH_3$			(c) $BO_3^{3-}$	$\Box$ (d) $CO_3^{2-}$		
	(c) $B_2H_6$ $\Box$ (d) $CO_2$		146.	In NO <sub>3</sub> ion, number of bo	nd pairs and lone	pairs of elect	rons
133.	Which of the following phenomenon will occur when t	wo		on nitrogen atom are:		[C.B.S.E. 2	2002]
	atoms of same spin will react?			(a) 2, 2	□ (b) 3, 1		
	(a) Bonding will not occur			(c) 1, 3	$\square$ (d) 4, 0		
	(b) Orbital overlap will not occur		147.	In OF <sub>2</sub> , number of bond		pairs of elect	rons
	(c) Both (a) and (b)			are:	F	[D.P.M.T. 2	
	(d) None of the above			(a) 2, 6	□ (b) 2, 8	<u></u>	
124				(c) 2, 10	(d) 1, 9		
134.	Which bond angle $\theta$ would result in the maximum dip	ore	148	A square planar comple		hybridizatio	
	moment for the triatomic molecule $XY_2$ ?	_	170,	which atomic orbitals?	in in initial by	[A.I.E.E.E. 2	
	(a) $\theta = 90^{\circ}$				□ (b) c = =		_
	(c) $\theta = 150^{\circ}$			(a) $s, p_x, p_y, p_z, d_{yz}$	$\Box  \text{(b) } s, p_x, p_y$		
135.	The structure of ICl <sub>2</sub> is:			(c) $s, p_x, p_y, d_z^2$	$\square  (d) \ s, p_x  , p_z$		
*	(a) trigonal		149.	Match List (I) (molecule			
	(b) octahedral		-	select the correct answer	using the codes	_	
					•	[S.C.R.A. 2	2000]

	List I List II		(c) $BF_3 > NF_3 > PF_3 > CIF_3$	
	I. Li <sub>2</sub> A. 3		(d) $BF_3 > ClF_3 > PF_3 > NF_3$	
	II. N <sub>2</sub> B. 1.5		[Hint: Bond angles are: BF3-120°, NF3-106°, PF3-1	101°,
	III. Be <sub>2</sub> C. 1.0		ClF <sub>3</sub> —90° ]	
	IV. O <sub>2</sub> D. 0	158.	In an octahedral structure, the pair of d-orbitals invol	ved
	E. 2		in $d^2sp^3$ hybridization is: [C.B.S.E. (P.M.T.) 20	004]
	Codes:		(a) $d_{x^2-y^2}$ , $d_{z^2}$	
	(a) I – B ; II – C; III – A; IV – E		(c) $d_2^2$ , $d_{xz}$ $\square$ (d) $d_{xy}$ , $d_{yz}$	
	(b) I – C; II – A; III – D; IV – E	159.	According to molecular orbital theory which of	the
	(c) $I - D$ ; $II - A$ ; $III - E$ ; $IV - C$		following statements about the magnetic character and be	
	(d) I - C; II - B; III - E; IV - A		order is correct regarding $O_2^{\dagger}$ ? [I.I.T. (S) 20	
150			(a) Paramagnetic and bond order $< O_2$	ر کر ک
150.	The correct order of hybridization of the central atom in		(b) Paramagnetic and bond order $> O_2$	
	the following species, NH <sub>3</sub> , [Pt(Cl <sub>4</sub> )] <sup>2-</sup> , PCl <sub>5</sub> and BCl <sub>3</sub> :		(c) Diamagnetic and bond order < O <sub>2</sub>	
	[I.I.T. (S) 2001; B.H.U. 2005]		•	П
	(a) $dsp^2$ , $dsp^3$ , $sp^2$ and $sp^3$	1/0	(d) Diamagnetic and bond order > O <sub>2</sub>	_
	(b) $sp^3$ , $dsp^2$ , $dsp^3$ , $sp^2$	160.	Which is the correct order of increasing dipole momer	ıτι
	(c) $dsp^2$ , $sp^2$ , $sp^3$ , $dsp^3$		(a) CIF < BrCl < NO < HCl < LII	ㅁ
	(d) $dsp^2$ , $sp^3$ , $sp^2$ , $dsp^3$		(b) LiI < BrCl < HCl < CIF < NO	
151.	The common features among the species CN <sup>-</sup> , CO and NO <sup>+</sup>		(c) BrCl < NO < HCl < ClF < LiI	
	are: [I.I.T. (S) 2001]	-	(d) NO < BrCl < HCl < Lil < ClF	_ ⊔
	(a) bond order three and isoelectronic		[Hint: Electronegativity Li = 1.0, H = 2.1, N = 3.0, O = 3.	.5,
	(b) bond order three and weak field ligand		F = 4.0, $CI = 2.9$ , $Br = 2.8$ , $I = 2.2$	
	(c) bond order two and $\pi$ -acceptors		Electronegativity difference BrCl = $0.1$ , NO = $0.5$ , HCl = $0.8$ , ClF = $1.1$ , LiI = $1.2$	
	(d) isoelectronic and weak field ligands		Dipole moment ∝ Electronegativity difference]	
152.	Which of the following molecular species has unpaired	161	Which of the following has highest melting point?	
	electron(s)? [I.I.T. (S) 2002]	101.	[P.E.T. (Raj.) 2	ഹവി
			(a) $BeCl_2$ $\Box$ (b) $MgCl_2$	[C00
	(a) $N_2$ $\square$ (b) $F_2$ $\square$		(c) $CaCl_2$ $\Box$ (d) $BaCl_2$	
	(c) $O_2^-$	162		വരാ
153.	Which of the following hydrocarbons has the lowest dipole	102.	Maximum bond angle is present in: [D.P.M.T. 2 (a) $BF_3$ $\Box$ (b) $BCl_3$	003
	moment? [I.I.T. (S) 2002]		· · · · · · · · · · · · · · · · · · ·	
•	CH <sub>3</sub> CH <sub>3</sub>	162	<del>-</del>	
	(a) >C <	163.	Pick out the isoelectronic structures from the followin	_
	H H		[A.M.U. 2	003
	(b) $CH_3-C\equiv C-CH_3$		(I) $CH_3^+$ (II) $H_3^+O$ (III) $NH_3$ (IV) $CH_3^-$ (a) I and II	
	(c) $CH_3-CH_2-C \equiv C-H$			Ц
	(d) $CH_2 = CH - C \equiv C - H$		(b) III and IV	
154.	The nodal plane in the $\pi$ -bond of ethene is located in:		(c) II, III and IV	닏
	[I.I.T. (S) 2002]	7.54	(d) III & IV and II, III & IV	
	(a) the molecular plane	164.	Which of the following is a correct set? [E.A.M.C.E.T. 2	
	(b) a plane parallel to molecular plane		(a) $H_2O sp^3$ angular	
	(c) a plane perpendicular to the molecular plane which		(b) $H_2O$ $sp^2$ linear	
	bisects the carbon-carbon sigma bond at right angle □		(c) $NH_4^+ dsp^2$ square planar	
	(d) a plane perpendicular to the molecular plane which		(d) CH <sub>4</sub> dsp <sup>2</sup> tetrahedral	
	contains the carbon-carbon σ-bonds	165.	Which of the following compounds has the smallest b	
155.	The shape of $O_2F_2$ is similar to: [A.I.I.M.S. 2004]		angle in its molecule? [A.I.E.E.E. 2	.003
	(a) $C_2F_2$ $\square$ (b) $H_2O_2$ $\square$		(a) $SO_2$ $\square$ (b) $H_2O$	
	(c) $H_2F_2$ $\square$ (d) $C_2H_2$ $\square$		(c) $H_2S$ $\square$ (d) $NH_3$	
156	The ONO angle is maximum in: [A.I.I.M.S. 2004]	166.	Which of the following pairs of molecules will h	nave
	(a) $NO_3^-$		permanent dipole moments for both members?	
	(c) $NO_2$		[A.I.E.E.E. 2	.003
	[Hint: In NO <sub>2</sub> , nitrogen atom is sp hybridized.]		(a) $SiF_4$ and $NO_2$ $\Box$ (b) $NO_2$ and $CO_2$	
157	The correct decreasing order of bond angles is:		(c) $NO_2$ and $O_3$ $\square$ (d) $SiF_4$ and $CO_2$	
	(a) $ClF_3 > PF_3 > NF_3 > BF_3$	167.	If the molecule of HCl is considered as totally polar,	, the
	(b) $BF_3 > PF_3 > NF_3 > CIF_3$		expected value of dipole moment is 6.12 D but	the
		•		

	experimental value of dipole mo	oment is 1.03D. What is the		of hybridization:		[C.E.]	E. (Kerala)	2004]
	percentage ionic character in H	Cl?		(a) BF <sub>3</sub> and NCl <sub>3</sub>		b) H <sub>2</sub> S and	BeCl <sub>2</sub>	
	(a) 17	o) 83 $\square$		(c) SF <sub>4</sub> and NCl <sub>3</sub>		d) NCl <sub>3</sub> and	$H_2S$	
	(c) 50	i) 90 $\square$	179.	Pair of species having is	dentica	l shapes for	molecules	is:
	obs. di	ipole moment					[D.C.E.	2005]
	[Hint: % ionic character = $\frac{\text{obs. di}}{\text{cal. di}}$	pole moment		(a) CF <sub>4</sub> , SF <sub>4</sub>		-	3	
	1.03	100 151		(c) $XeF_2$ , $CO_2$	-	d) PF <sub>5</sub> , IF <sub>5</sub>		
	$=\frac{6.12}{6.12}$	100 = 17 ]		[Hint: Both XeF <sub>2</sub> and CO		-		
168.	Which of the following shows	isostructural species?	180.	The <i>d</i> -orbital involved in	n sp³d	•		
		[A.F.M.C. 2003]		• •			E.T. (J&K)	2005]
	(a) $NH_4^+$ and $NH_2^ \square$ (b)	o) $CH_3^-$ and $CH_3^+$	,	(a) $d_x^2 - y^2$		b) $d_{xy}$		
	(c) $SO_4^{2-}$ , $PO_4^{3-}$ and $BF_4^ \square$ (d)	d) $NH_4^+$ and $NH_3$		(c) $d_z^2$		d) $d_{zx}$		
169.	The ion which is not tetrahedra	al in shape is:	181.	Which of the following	-		E.T. (J&K)	_
	•	[A.I.I.M.S. 2003]		(a) XeF <sub>2</sub>		b) XeO <sub>3</sub> F		
	(a) BF <sub>4</sub>	o) NH <sub>4</sub> <sup>+</sup>	100	(c) XeO <sub>2</sub> F <sub>2</sub>		d) XeF <sub>4</sub>		
	(c) $[Cu(NH_3)_4]^{2+}$		182.	The species having bond	order	different fro		
170	Which of the following has dsp	<del>.</del>			·		[I.I.T.	
170.	viden of the following has not	[P.E.T. (M.P.) 2003]		(a) NO		b) NO <sup>+</sup>		
	(a) NiCl <sup>2</sup> -			(c) CN		d) N <sub>2</sub>		
	(a) $\operatorname{NiCl}_{4}^{2-}$ $\square$ (b) (c) $\operatorname{NH}_{4}^{4}$ $\square$ (c)	d) PtCl <sup>2-</sup>	183.	Which of the following	speci	es exhibits	•	_
	In which of the following pair	,	1	behaviour?	,,,,,,	n > 0.2-	[A.I.E.E.E.	
	order three and are isoelectron			(a) NO		(b) O <sub>2</sub> <sup>2-</sup>	•	
		b) $NO^+$ , $CO^+$	1	(c) O <sub>2</sub> <sup>+</sup>		(d) O <sub>2</sub>		
	(c) $CN^-$ , $O_2^+$	d) CO. O <sub>2</sub>	184.	The charge/size ratio of			-	-
172.	Paramagnetism of oxygen is ex			power. Which one of t				
		[P.E.T. (Kerala) 2003]		the increasing order of t				
	(a) $(2\sigma p_x)^1 (2\pi p_y)^1$			species K <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> ,			[A.I.E.E.E.	-
	(c) $(2\sigma p_z)^1 (2\pi p_y)^1$	d) $(2\pi p_{\nu})^{1}(2\pi p_{\nu})^{1}$		(a) $Ca^{2+} < Mg^{2+} < Be^{2+}$				
172	Which of the following is not $Q$	· ·		(b) $Mg^{2+} < Be^{2+} < K^+ <$			•	
175.		.A.M.C.E.T. (Medical) 2004]		(c) $Be^{2+} < K^+ < Ca^{2+} < 1$				
	(a) One of the favourable cond		105	(d) $K^+ < Ca^{2+} < Mg^{2+} <$			11	. —
• .	cation is low ionisation po		100.	In which of the follow				
	(b) Coordination number of Cs	· •		order has increased and	ine m	agneuc pow	IA.I.E.E.E.	
	(c) Ionic bond is directional	, in eser is o		(a) $N_2 \longrightarrow N_2^+$		(b) C	-	2007]
	(d) Ionic compounds have high			(c) NO $\longrightarrow$ NO <sup>+</sup>		(d) $\Omega_2 \longrightarrow$	$O_2^{\pm}$	
	(a) toric compounds have high		1	In which of the follo				
174.	Covalent bond exists in:	[D.C.E. 2004]		structural?	wing 1	pans, two	[C.B.S.E.	
		b) AlCl <sub>3</sub>		(a) $SO_3^{2-}$ and $NO_3^{-}$	п	(b) BF <sub>3</sub> and		
		d) MgCl <sub>2</sub> □		(c) $BrO_3^-$ and $XeO_3$		(d) $SF_4$ and		
175.	In which of the following the	=	187.	Match List I with List				
	number of lone pair of electro		i	codes from the choices			T. (Kerala)	
	-	b) XeF <sub>4</sub>		List I	List II		(2	,
		d) I <sub>3</sub>			Linear			
176.	Bond energies in NO, NO+ and	NO are such as:	-	-	Pyram			-
	. •	[C.E.T. (Punjab) 2004	-	· .		al bipyram	idal	
	(a) $NO^- > NO > NO^+$	b) NO > NO <sup>-</sup> > NO <sup>+</sup>			Tetrah			
	(c) $NO^+ > NO > NO^-$	d) $NO^+ > NO^- > NO$		₹ .		onal bipyra	amidal	
177.	Molecular orbital electronic con	nfiguration for $'x'$ anion is			Angul			
	$KK^* (\sigma 2s)^2 (\mathring{\sigma} 2s)^2 (\pi 2p_x)^2 (\pi 2p_x)^2$			(a) A-3, B-5, C-2, D-1,	~		,	
	The anion 'x' is:	[A.M.U. 2004		(b) A-3, B-5, C-4, D-1,				
	(a) $N_2^-$	b) O <sub>2</sub>		(c) A-3, B-5, C-6, D-1,				
	(c) $N_2^{2-}$	(d) $O_2^{2-}$		(d) A-3, B-5, C-2, D-6,				
178.	Among the compounds BF <sub>3</sub> ,	NCl <sub>3</sub> , SF <sub>4</sub> , H <sub>2</sub> S and BeCl <sub>2</sub>		(e) A-3, B-5, C-2, D-4,				
	identify the one in which the cer			*				

188.	Which of the following is paramagnetic with bond order 0.5? [P.E.T. (Kerala) 2007] (a) $F_2$ $\Box$ (b) $H_2^+$ $\Box$	(a) Antibonding π-molecular orbital (b) Bonding π-molecular orbital (c) σ-bonding molecular orbital
	(a) $F_2$ $\Box$ (b) $H_2^+$ $\Box$ (c) $N_2$ $\Box$ (d) $O_2^ \Box$	(c) σ-bonding molecular orbital (d) σ-antibonding molecular orbital
1 2 Q	Among the following, the pair in which the two species are	196. Four diatomic species are listed below in different
102.	not isostructural is: [P.E.T. (Kerala) 2007]	sequences. Which of these represents the correct order of
	(a) $IO_3$ and $XeO_3$ $\square$ (b) $PF_6$ and $SF_6$ $\square$	increasing bond order? [C.B.S.E. 2008]
	(c) $BH_4$ and $NH_4^+$ $\Box$ (d) $CO_3^-$ and $NO_2^ \Box$	(a) $C_2^2 < \text{He}_2^4 < \text{NO} < O_2^2$
	[Hint: $CO_3^2$ — Trigonal planar; $NO_2$ — Angular]	(a) $C_2 < RC_2 < RO < C_2$ (b) $He_2^+ < O_2^- < RO < C_2^2$
190	The correct order of bond order values among the following	(c) $O_2^2 < NO < C_2^2 < He_2^+$
170.	is: [P.M.T. (Kerala) 2007]	(d) NO $<$ $C_2^2 <$ $O_2^2 <$ $He_2^4$
	(i) NO <sup>-</sup> (ii) NO <sup>+</sup> (iii) NO (iv) NO <sup>2+</sup> (v) NO <sup>2-</sup>	[Hint: Bond order He <sub>2</sub> <sup>+</sup> = 0.5; O <sub>2</sub> <sup>-</sup> = 1.5; NO = 2.5; C <sub>2</sub> <sup>2</sup> = 3]
	(a) (i) $<$ (ii) $<$ (iii) $<$ (i) $<$ (v)	197. Which one of the following pairs of species has the same
	(b) $(iv) = (ii) < (i) < (v) < (iii)$	bond order? [A.I.E.E.E. 2008]
	(c) $(v) < (i) < (iv) = (iii) < (ii)$	(a) $NO^+$ and $CN^ \square$ (b) $CN^-$ and $NO^+$ $\square$
	(d) (v) < (i) < (iv) < (iii) < (ii)	(c) $CN^-$ and $CN^+$ $\square$ (d) $O_2^-$ and $CN^ \square$
191	The bond lengths and bond angles in the molecules of	[Hint: CN and NO+ are isoelectronic. Both have 14 electrons
1/1.	methane, ammonia and water are given below:	each.]
	and the second s	198. The calculated bond order of superoxide ion (O <sub>2</sub> ) is:
	$C_{>0.109 \text{ nm}}$ $N_{>0.101 \text{ nm}}$ $O_{>0.096 \text{ nm}}$	[C.E.T. (Karnataka) 2008]
	100.50	(a) 1.5
	H 109.5° H H 107° H H 104.5° H	(c) 2.5
	This variation in bond angle is a result of	199. Molecular shapes of SF <sub>4</sub> , CF <sub>4</sub> and XeF <sub>4</sub> are:
	(i) the increasing repulsion between hydrogen atoms as	[P.M.T. (Kerala) 2008]
	the bond length decreases	(a) the same with 1, 1 and 1 lone pair of electrons
	(ii) the number of non-bonding electron pairs in the	respectively on the central atom $\Box$
	molecule	(b) the same with 1, 0 and 2 lone pairs of electrons
	(iii) a non-bonding electron pair having a greater repulsive	respectively on the central atom
	force than a bonding electron pair.	(c) different with 0, 1 and 2 lone pairs of electrons
	[P.M.T. (Kerala) 2007]	respectively on the central atom
	(a) (i), (ii) and (iii) are correct	(d) different with 2, 0 and 1 lone pairs of electrons
	(b) (i) and (ii) are correct	respectively on the central atom
	(c) (ii) and (iii) are correct	(e) different with 1, 0 and 2 lone pairs of electrons
	(d) (i) only is correct $\Box$	respectively on the central atom
192.	Match the compounds in the List I with that in List II:	200. Which of the following does not have a coordinate bond?  [C.P.M.T. 2008]
	List I List II	(a) $SO_2$
	A. XeO <sub>3</sub> i. Planar triangular	(c) $H_2SO_3$
	B. XeOF <sub>4</sub> ii. T-shape	201. Which of the following represents the Lewis structure of
	C. BO <sub>3</sub> iii. Trigonal pyramid	N <sub>2</sub> molecule? [A.F.M.C. 2008]
	D. ClF <sub>3</sub> iv. Square pyramid	···
	E. $I_3(aq)$ v. Linear	(a) $\stackrel{\times}{\times} N \equiv N \stackrel{\times}{\times}$ $\square$ (b) $\stackrel{\times}{\times} N \stackrel{\times}{=} N \stackrel{\times}{\times}$ $\square$
	vi. Bent [P.M.T. (Kerala) 2007]	
	(a) A-i, B-iv, C-iii, D-ii, E-v □ (b) A-ii, B-iv, C-i, D-iii, E-vi □	202. Shape and hybridization of $\text{IF}_5$ respectively are:
	(b) A-ii, B-iv, C-i, D-iii, E-vi (c) A-iii, B-iv, C-i, D-ii, E-vi □	[J.E.E. (Orissa) 2008]
	and the second of the second o	(a) trigonal bipyramidal, $sp^3d$
103	(d) A-iii, B-iv, C-i, D-ii, E-v  Which of the following two are isostructural?	(b) see-saw, $sp^3d$ .
193	[B.H.U. 2007]	(c) square pyramidal, $sp^3d^2$
	(a) $XeF_2$ , $IF_2^ \Box$ (b) $NH_3$ , $BF_3$ $\Box$	(d) pentagonal pyramidal, $sp^3d^2$
	(a) $Xe_{12}$ $H_{2}$ (b) $Ye_{13}$ , $E_{13}$ (c) $CO_{3}^{2}$ , $SO_{3}^{2}$ $\Box$ (d) $PCl_{5}$ , $ICl_{5}$ $\Box$	203. Cl—P—Cl bond angles in PCl <sub>5</sub> molecule are :
194	Planar structure is shown by: [A.I.I.M.S. 2007]	
*/7	(a) $CO_3^{2-}$ $\Box$ (b) $BCl_3$	(a) 120° and 90°
	(c) $N(SiH_3)_3$ $\square$ (d) all of these $\square$	(c) 60° and 120°
195	N <sub>2</sub> accepts electron and converts into $N_2$ , where the electron	
	goes? [D.C.E. (Engg.) 2007]	
	<i>(</i>	[C.B.S.E. (P.M.T.) 2009]

	(a) $N_2^{2-} < N_2^{-} < N_2$	[Hint: The B.O. of both $H_2^+$ and $H_2^-$ are 1/2 but $H_2^+$ is more stated as it does not have antibonding electron.]	ble
	[Hint: B.O. $N_2 = \frac{10-4}{2} = 3$ ; B.O. $N_2 = \frac{10-5}{2} = 2.5$ ;	211. Arrange the following in the increasing order of their bo order: O <sub>2</sub> , O <sub>2</sub> , O <sub>2</sub> and O <sub>2</sub> . [C.E.T. (Karnataka) 20	
	B.O. $N_2^{2-} = \frac{10-6}{2} = 2.0$ ]	(a) $O_2^{2-}$ , $O_2^-$ , $O_2^+$ , $O_2$ $\Box$ (b) $O_2^+$ , $O_2$ , $O_2^-$ , $O_2^{2-}$	
205.	In which of the following molecules/ions BF <sub>3</sub> , NO <sub>2</sub> , NH <sub>2</sub>		
	and $H_2O$ , the central atom is $sp^2$ hybridised?  [C.B.S.E. (P.M.T.) 2009]	[Hint: B.O. of $O_2 = \frac{10-6}{2} = 2.0$ ; B.O. of $O_2^+ = \frac{10-5}{2} = 2.5$ ;	
	(a) $NH_2^-$ and $H_2O$ $\square$ (b) $NO_2^-$ and $H_2O$ $\square$	B.O. of $O_2^- = \frac{10-7}{2} = 1.5$ ; B.O. of $O_2^{2-} = \frac{10-8}{2} = 1$ ]	
	(c) $BF_3$ and $NO_2$ $\square$ (d) $NO_2$ and $NH_2$ $\square$		•
	[Hint: BF <sub>3</sub> $\longrightarrow sp^2$ ; NO <sub>2</sub> $\longrightarrow sp^2$ ; NH <sub>2</sub> $\longrightarrow sp^3$ ; H <sub>2</sub> O $\longrightarrow sp^3$ ]	212. Out of $N_2O$ , $SO_2$ , $I_3^+$ , $I_3^-$ , $H_2O$ , $NO_2^-$ and $N_3^-$ , the linear specare : [J.E.E. (Orissa) 20	
206.	The correct stability order of the following resonance	(a) $NO_2^2$ , $I_3^4$ , $H_2O$	נכע ר
	structures is: [I.I.T. 2009]	(c) $N_2O$ , $I_3$ , $N_3$	
	(i) $H_2C = N = N$ (ii) $H_2C - N = N$	213. The energy required to break one mole of Cl—Cl bonds	in
	(iii) $H_2\bar{C} - \stackrel{+}{N} = N$ (iv) $H_2\bar{C} - N = \stackrel{+}{N}$	Cl <sub>2</sub> is 242 kJ mol <sup>-1</sup> . The longest wavelength of light capa	
	(a) (i) $>$ (ii) $>$ (iv) $>$ (iii) $\square$ (b) (i) $>$ (ii) $>$ (iv) $\square$	of breaking a single Cl—Cl bond is: [A.I.E.E.E. 20	10]
	(c) (i) > (iii) > (iii) > (iv) $\square$ (d) (iii) > (i) > (iv) > (ii) $\square$	$[c = 3 \times 10^8 \text{ ms}^{-1} \text{ and } N_A = 6.02 \times 10^{23} \text{ mol}^{-1}]$	
	[Hint : Number of $\pi$ -bonds $\infty$ Resonance energy $\infty$ stability	(a) 494 nm	
	In contributing structures, like charges should not reside	(c) 640 nm	.3
	on atoms closer to each other and unlike charges should not be widely separated.]	[Hint : Energy required to break one bond of Cl—Cl = $\frac{242 \times 10}{N_A}$	_J
207.	Using MO theory predict which of the following species has	$=\frac{242\times10^3}{6.02\times10^{23}}$	
	the shortest bond length? [A.I.E.E.E. 2009]	6.02 × 10	
	(a) $O_2^{2+}$	Applying the formula, $E = \frac{hc}{\lambda}$ or $\lambda = \frac{hc}{E}$	
		$= \frac{6.63 \times 10^{-34} \times 3 \times 10^8 \times 6.02 \times 10^8}{10^{-34} \times 3 \times 10^8 \times 6.02 \times 10^8}$	) <sup>23</sup>
	[Hint: Bond length $\propto \frac{1}{\text{Bond order}}$ ; B.O. of $O_2^{2+}$ , $O_2^+$ , $O_2^-$ and $O_2^{2-}$	$= \frac{6.63 \times 10^{-34} \times 3 \times 10^8 \times 6.02 \times 10^8}{242 \times 10^3}$ $= 494 \times 10^{-9} \text{ m} = 494 \text{ nm}$	
	are 3.0, 2.5, 1.5 and 1 respectively.]	214. In which of the following molecules, the central atom d	
208.	The bond dissociation energy of B—F in BF <sub>3</sub> is 646 kJmol <sup>-1</sup>	not have $sp^3$ -hybridization? [C.B.S.E. (P.M.T.) 20	
	whereas that of C—F in CF <sub>4</sub> is 515 kJ mol <sup>-1</sup> . The correct reason	(a) $CH_4$ $\Box$ (b) $SF_4$	
	for higher B—F bond dissociation energy as compared to that of C—F is: [A.I.E.E. 2009]	(c) $BF_4^ \Box$ (d) $NH_4^+$	
	(a) smaller size of B atom as compared to that of C atom $\Box$	215. Some of the properties of two species $NO_3^-$ and $H_3O^+$	are
	(b) stronger $\sigma$ bond between B and Fin BF <sub>3</sub> as compared to that	described below. Which one of them is correct?	
	between C and F in CF <sub>4</sub>	[C.B.S.E. (P.M.T.) 20	
	(c) significant $p\pi$ - $p\pi$ interaction between B and F in BF <sub>3</sub>	(a) Dissimilar in hybridization for the central atom w different structures	ntn
	whereas there is no possibility of such interaction	(b) Isostructural with same hybridization for the cen	tral
	between C and F in $CF_4$	atom	
	(d) lower degree of $p\pi$ - $p\pi$ interaction between B and F in	(c) Isostructural with different hybridization for the cen	tral
	BF <sub>3</sub> than that between C and F in CF <sub>4</sub> [Hint: In BF <sub>3</sub> , B is $sp^2$ hybridized and has a vacant $2p$ orbital	atom	
	which overlaps laterally with a filled $2p$ orbital of F	(d) Similar in hybridization for the central atom w	rith
	forming strong $p\pi$ - $p\pi$ bond. However, in $CF_4$ the $C$ does	different structures	
	not have any vacant p-orbital.]	[Hint: NO <sub>3</sub> has $sp^2$ hybridization while H <sub>3</sub> O <sup>+</sup> has $sp^3$ hybridization]	idi-
209.	A covalent molecule AB <sub>3</sub> has pyramidal structure. The	216. The bond energy (in kcal mol <sup>-1</sup> ) of a C—C single bond	1 is
	number of lone pair and bond pair electrons in the molecule	approximately: [I.I.T. 20	
	are respectively: [C.E.T. (Karnataka) 2009] (a) 0 and 4 $\square$ (b) 3 and 1 $\square$	(a) 1	
	(c) 1 and 3	(c) 100	
<b>2</b> 10.	The correct statement with regard to $H_2^+$ and $H_2^-$ is:	217. The species having pyramidal shape is: [I.I.T. 20]	)10]
	[C.E.T. (Karnataka) 2009]	(a) $SO_2$	
	(a) both $H_2^+$ and $H_2^-$ do not exist	(c) $SiO_3^2$	
	(b) $H_2^-$ is more stable than $H_2^+$	218. In which of the following pairs of molecules/ions,	the
	(c) $H_2^+$ is more stable than $H_2^-$	central atoms have sp <sup>2</sup> -hybridization? [C.B.S.E. (P.M.T.) Prel. 20	11 (L)
	(d) both $H_2^+$ and $H_2^-$ are equally stable	[C.D.S.E. (F.IVI.T.) FTel. 20	)1V]

	(a) NO <sub>2</sub> and NH <sub>3</sub> (c) NH <sub>2</sub> and H <sub>2</sub> O		(b) BF <sub>3</sub> and NO <sub>2</sub> (d) BF <sub>3</sub> and NH <sub>2</sub>		227. $N_2$ and $O_2$ are converted to monopositive cations $N_2^+$ and $O_2^+$ respectively. Which is incorrect? [P.E.T. (Kerala) 2010]
219	Which one of the follow				(a) In $N_2^+$ , the N—N bond is weakened
217.	normal conditions?	vii.g	[C.B.S.E. (P.M.T.) Prel		(b) In $O_2^+$ , the bond order increases
			the state of the s	0.00	(c) In $O_2^2$ , the paramagnetism decreases
	(a) Be <sub>2</sub> <sup>+</sup>		(b) Be <sub>2</sub>		_ , _ ,
222	(c) B <sub>2</sub>		(d) Li <sub>2</sub>	, 🗆	(d) N <sub>2</sub> <sup>+</sup> becomes diamagnetic
220.	In which one of the follo				(e) Both $O_2$ and $O_2^+$ are paramagnetic
	the type of hybridization	ı wn			[Hint: M.O. configuration of N <sub>2</sub> :
	the other three?		[C.B.S.E. (P.M.T.) Prel		$(\sigma 1s)^2 (\mathring{\sigma} 1s)^2 (\sigma 2s)^2 (\mathring{\sigma} 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2$ , B.O. $=\frac{10-4}{2}=3$
	(a) SF <sub>4</sub>		(b) $I_3^-$		
	(c) SbCl <sub>5</sub>	. 🗆	(d) PCl <sub>5</sub>		M.O. configuration of $N_2^+$ :
	[Hint: In SF <sub>4</sub> , S has dsp <sup>3</sup>				$(\sigma 1s)^2 (\mathring{\sigma} 1s)^2 (\sigma 2s)^2 (\mathring{\sigma} 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^1$ B.O. $= \frac{9-4}{2} = 2.5$
	In $I_3$ , I has $dsp^3$ h	ybrid	ization		M.O. configuration of $O_2$ :
	In PCl <sub>5</sub> , P has dsp	<sup>3</sup> hyl	bridization		
	In SbCl <sub>5</sub> , Sb has s				$(\sigma 1s)^2 (\sigma 1s)^2 (\sigma 2s)^2 (\sigma 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi 2p_x)^1 (\pi 2p_y)^1$
221.	The bond order of CO r	nole	cule is: [J.E.E. (W.B.	2010]	B.O. $=\frac{10-6}{2}=2$
	(a) 2		(b) 2.5		<b>4</b>
	(c) 3		(d) 3.5		M.O. configuration of $O_2^+$ :
222.	For which element the	inert	ness of the electron pa	ir will	$(\sigma 1s)^2 (\sigma 1s)^2 (\sigma 2s)^2 (\sigma 2s)^2 (\sigma 2p_x)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi 2p_x)^1 (\pi 2p_y)^0$
	not be observed?		[J.E.E. (W.B.		• • • • • • • • • • • • • • • • • • • •
	(a) Sn		(b) Fe		B.O. $=\frac{10-5}{2}=2.5$
	(c) Pb		(d) In		Bond order ∝ Bond energy ∝ strength of the bond]
223.	Non-zero dipole momer	nt is	shown by:		228. A neutral molecule XF <sub>3</sub> has a zero dipole moment. The
			[J.E.E. (Orissa	2010]	element X is most likely : [P.E.T. (Kerala) 2010]
	(a) CCl <sub>4</sub>		(b) CO <sub>2</sub>		(a) chlorine $\Box$ (b) boron $\Box$
			Cl		(c) nitrogen
	(c) H <sub>2</sub> O	П	(d)	□.	229. Match the following:
*	(C) 112O		(a) Ci	· ·	List-II List-II
224.	Which of the following	has	a regular geometry?		(Molecule) (Number of lone pairs
			[J.E.E. (Orissa	20101	on central atom)
	(a) CHCl <sub>3</sub>		(b) SF <sub>4</sub>		(A) NH <sub>3</sub> (i) Two
	(c) XeF <sub>6</sub>		(d) PCl <sub>5</sub>		(B) H <sub>2</sub> O (ii) Three
225.	Which of the following		· · · · · · · · · · · · · · · · · · ·		(C) XeF <sub>2</sub> (iii) Zero
			[A.M.U. (Engg	) 2010]	(D) CH <sub>4</sub> (iv) Four
	(a) $A1F_6^{3-}$		(b) $CoF_6^{3-}$		(v) One
	(c) BF <sub>6</sub> <sup>3-</sup>		(d) SiF <sub>6</sub> <sup>2-</sup>		The correct answer is: [E.A.M.C.E.T. (Engg.) 2010]
226	Which of the following		_		(A) (B) (C) (D)
220	winch of the following	Stati	[P.E.T. (Kerala	Loroc &	(a) (v) (i) (iii) [
	(a) H <sub>2</sub> molecule has on	o cio		. ZUIU)	(b) (iii) (i) (ii) (v)
		_			(c) (v) (i) (ii) (iii)
	(b) HCl molecule has o		•		(d) (i) (v) (iii) (iv)
	(c) water molecule has	two	sigma bonds and two lor	ie pairs	
	(d) Tabelous moderate 1	' L	Erro siamo handa and		
	(d) Ethylene molecule l	nave	nve sigma bonds and	one pi	[Hint: N O Xe: C ]
	bond	: 1.	and and there siems I	الله مد	HUH H H H HH
	(e) Acetylene has timee	pro	onds and three sigma b	onusLi	п г п
Se	t II: This set contai	ins	questions with tw	o or m	ore correct answers.
230	. Which of the following	hav	e identical bond order?		(c) cis-3-hexene
	Ö			. 1992]	(d) 2, 2, 3, 3-tetramethylbutane
					· · ·
	(a) CN <sup>-</sup>		(b) O <sub>2</sub>	, 🗆	232. Species having same bond order are:
			<del>-</del> .	. 🗆	232. Species having same bond order are:  (a) $N_2$
231	(a) CN <sup>-</sup> (c) NO <sup>+</sup> . The molecules that wil		(d) CN <sup>+</sup>		
231	(c) NO <sup>+</sup>	□ l hav	(d) CN <sup>+</sup>		(a) $N_2$ $\square$ (b) $N_2^+$ $\square$
231	(c) NO <sup>+</sup> . The molecules that wil	□ l hav	(d) CN <sup>+</sup>	□ [. 1992]	(a) $N_2$

234.	Molecules having distorted geometry are: (a) $H_2O$ $\square$ (b) $NH_3$ $\square$	242. Which of the following molecules have a bond angle smaller than tetrahedral bond?
	(c) $N_3H$ $\square$ (d) $XeF_2$ $\square$	(a) NH <sub>4</sub>
225	The linear structure is assumed by: [I.I.T. 1991]	(c) $NH_3$
200.	(a) $SnCl_2$ $\Box$ (b) $NCO^ \Box$	1
		243. Identify the species which are non-planar:
226	(c) $NO_2^+$	(a) $CH_3^+$
236.	Which of the following hybridization results in non-planar	(c) $BF_4$
	orbitals?	244. The nitrogen oxide(s) that contain(s) N—N bond(s) is (are)
	(a) $sp^3$	[LI.T. 2009]
		(a) $N_2O$ $\square$ (b) $N_2O_3$ $\square$
237.	Which statement(s) is/are correct?	(c) $N_2O_4$
	(a) A sigma bond is stronger than $\pi$ -bond	$[\mathbf{Hint}: N_2O: N=N=O\longleftrightarrow N=N-O$
	(b) A sigma bond is weaker than $\pi$ -bond	
	(c) Hydrogen bonding is weaker than covalent bonding	$N_2O_3: N_2O_3$
	(d) A triple bond is weaker than double bond	N.O. N. N. O
238.	Which combination of the compounds and their geometry	$N_2O_3: \stackrel{O}{\longrightarrow} N-N \stackrel{O}{\longrightarrow} O$ $N_2O_4: \stackrel{O}{\longrightarrow} N-N \stackrel{O}{\longrightarrow} O$
	are correct?	245. Molecules with see-saw shape are :
	(a) $HgCl_2$ – linear $\Box$ (b) $ClF_3$ – V-shaped $\Box$	(a) $XeOF_4$ $\Box$ (b) $SF_4$
	(c) $ClF_3$ – T-shaped $\Box$ (d) $ICl_4$ – square planar $\Box$	(c) $XeOF_2$
239.	In the following case(s), hybridization of the underlined	246. The molecules in which the central atom is $sp^3d^2$ hybridisec
	atom is affected:	are:
	(a) $\underline{PCl}_5$ (solid) dissociates into $PCl_4^+$ and $PCl_6^-$	(a) $XeF_4$ $\Box$ (b) $XeF_6$
	(b) LiH reacts with <u>Al</u> H <sub>3</sub> forming LiAlH <sub>4</sub> □	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
	(c) NH <sub>3</sub> is protonated	247. Which of the following elucidate molecular orbital theor
	(d) H <sub>3</sub> PO <sub>2</sub> is heated forming PH <sub>3</sub> and H <sub>3</sub> PO <sub>3</sub>	rightly?
240.	sp <sup>3</sup> hybridization is present in:	(a) Number of MO's are equal to the number of AO's from
	(a) $SO_4^{2-}$ $\Box$ (b) $C_2H_2$ $\Box$	which they are formed
	(c) $BO_3^{3-}$	1
241.	Which of the following has tetrahedral structure and the	(b) BMO's increase electron density between the nuclei [
	central atom is sp <sup>3</sup> hybridized?	(c) Abivios have a region of zero electron density
	(a) $BF_4^ \Box$ (b) $IF_4^ \Box$	(d) Number of electrons in BMO's are more than in ABMO'
	(c) $SiH_4$ $\Box$ (d) $PF_4^ \Box$	
		·

4	uswe	ers.																	
12.56			(4)		(.)	4	<i>(</i> <b>L</b> )	-	(-)		f-1	-	(-)		(1-)		(-)	10	(.)
	(a)		(d)		(c)		(b)		(c)		(a)	7.			(b)		(c)	10.	
11.		12.		13.		14.		15.		16.		17.		18.		19.		20.	*
21.	(b)	22.	(c)	23.	(a)	24.	(c)	25.	(d)	26.	(d)	27.	(b) <sub>.</sub>	28.	(b)	29.	(a)	30.	(a)
31.	(a)	32.	(b)	33.	(d)	34.	(b,c)	35.	(b)	.36.	(a)	37.	(a)	38.	(b)	39.	(c)	40.	(b)
41.	(a)	42.	(b)	43.	(d)	44.	(c)	45.	(d)	46.	(c)	47.	(a)	48.	(a)	49.	(a)	50.	(b)
51.	(c)	52.	(d)	53.	(a)	54.	(b)	55.	(d)	56.	(b) ·	57.	(c)	58.	(c)	59.	(b)	60.	(d)
61.	(b) ·	62.	(b)	63.	(d)	64.	(c)	65.	(b)	66.	(d)	67.	(c)	68.	(c)	69.	(b)	70.	(a)
71.	(b)	72.	(b)	73.	(c)	74.	(d)	75.	(a)	76.	(c)	77.	(d)	78.	(d)	79.	(b)	80.	(a) '
81.	(d)	82.	(a)	83.	(c)	84.	(d)	85.	(b)	86.	(d)	87.	(b)	88.	(b)	89.	(c)	90.	(b)
91.	(d)	92.	(d)	93.	(d)	94.	(b)	95.	(d)	96.	(c)	97.	(d)	98.	(d)	99.	(a)	100.	(a)
101.	(c)	102.	(a)	103.	(b)	104.	(b) -	105.	(c)	106.	(d)	107.	(d)	108.	(c)	109.	(b)	110.	(d)
111.	(c)	112.	(b)	113.	(c)	114.	(a)	115.	(a)	116.	(d)	117.	(d)	118.	(b)	119.	(b)	120.	(c)
121.	(b)	122.	(a)	123.	(d)	124.	(c)	125.	(a)	126.	(d)	127.	(b)-	128.	(d)	129.	(b)	130.	(a)
131.	(a)	132.	(c)	133.	(c)	134.	(a)	135.	(d)	136.	(b)	137.	(d)	138.	(a)	139.	(b)	140.	.(c)
141.	(d)	142.	(d)	143.	(d)	144.	(c)	145.	(b)	146.	(d)	147.	(b)	148.	(b)	149.	(b)	150.	(b)
151.	(a)	152.	(c)	153.	(b)	154.	(a) ·	155.	(b)	156.	(b)	157.	(c)·	158.	(a) ·	159.	(b)	160.	(c)
161.	(d)	162.	(d)	163.	(d)	164.	(a)	165.	(c)	166.	(c)	167.	(a)	168.	(c)	169.	(c)	170.	(b)
171.	(a)	172.	(d)	173.	(c)	174.	(b) ·	175.	(d)	176.	(c)	177.	(a)	178.	(d)	179.	(c)	180.	(c)
181.	(d)	182.	(a)	183.	(b)	184.	(d)	185.	(c)	186.	(c)	187.	(d)	188.	(b)	189.	(d)	190.	(c)
191.	(c)	192.	(d)	193.	(a)	194.	(d)	195.	(a)	196.	(b)	197.	(b)	198.	(a)	199.	(e)	200.	(d)
201.	(a)	202.	(c)	203.	(a)	204.	(a)	205.	(c)	206.	(b)	207.	(a)	208.	(c)	209.	(c)	210.	(c)
211.	(d)	212.	(c)	213.	(a)	214.	(b)	215.	(a)	216.	(c)	217.	(d)	218.	(b)	219,	(b)	220.	(c)
221.	(c)	222.	(b)	223.	(c)	224.	(a)	225.	(c)	226.	(e)	227.	(d)	228.	(b)	229.	(c)	230.	(a,c)
231.	(b,c)	232.	(b,c)	233.	(a,b)	234.	(a,b,c,d)	235.	(b,c,d)	236.	(a,d)		(a,c)	238.	(a,c,d)		(a,b)		(a,d)
241.	(a,c,d)		(c,d)	243.	(b,c)	244.	(a,b,c)	245.	(b,d)	246.	(a,c).		(a,b,c)		•				

# **Objective Questions for IIT ASPIRANTS**



- Which of the following halides has different bond lengths?
  - (a) BCl<sub>3</sub>

(b) CC1<sub>4</sub>

(c) BeC1<sub>2</sub>

(d) PC15

[Hint: PCl5 has two types of bonds axial and equatorial. These two types of bonds have different bond lengths.]

- Which among the following has highest boiling point?

(b) He

(c) Ne

(d) Xe

[Hint: Xenon has highest boiling point because it has maximum van der Waals' forces due to the possession of more

- In which solvent NaCl has maximum solubility?
  - (a)  $H_2O$

(b) C<sub>2</sub>H<sub>5</sub>OH

(c) CH<sub>3</sub>COCH<sub>3</sub>

- (d) C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>
- [Hint: NaCl is an ionic compound. Solubility of an ionic compound depends on the value of dielectric constant of the solvent. Higher the value of dielectric constant of the solvent more is the solubility of the ionic compound.

Solvent Dielectric constant 80

H<sub>2</sub>O C<sub>2</sub>H<sub>5</sub>OH CH<sub>3</sub>COCH<sub>3</sub>

C2H5OC2H5

- Which has maximum covalent character?
- (a) NaCl

(b) SiCl<sub>4</sub>

(c) AICl<sub>3</sub>

(d) MgCl<sub>2</sub>

[Hint: Polarisation in the molecule increases with increase of charge and decreases in size of the cation when the anion

- 5. If  $\mu_1$  and  $\mu_2$  are the two dipole moments in the molecule with an angle  $\theta$  between them, then the resultant dipole moment will be:
  - (a)  $\mu = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta$
  - (b)  $\mu = \mu_1^2 + \mu_2^2 2\mu_1\mu_2 \cos \theta$
  - (c)  $\mu = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta)^{\frac{1}{2}}$
  - (d)  $\mu = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta)^{\frac{1}{3}}$
- The dipole moment of HBr is  $2.6 \times 10^{-30}$  cm and the interatomic spacing is 1.41 Å. The percentage of ionic character in HBr is:
  - (a) 10.5

(b) 11.5

(c) 12.5

(d) 13.5

Observed dipole moment [Hint:% ionic character = Theoretical dipole moment

Theoretical dipole moment of a 100% ionic character  $= e \times d = (1.6 \times 10^{-19} \text{C}) \times (1.41 \times 10^{-10} \text{ m})$  $= 2.256 \times 10^{-29}$  cm]

- 7. The boiling point of p-nitrophenol is higher than that of onitrophenol because:
  - (a) p-nitrophenol has intermolecular hydrogen bonding while o-nitrophenol has intramolecular hydrogen
  - (b) p-nitrophenol has intramolecular hydrogen bonding while o-nitrophenol has intermolecular hydrogen bonding.
  - (c) -NO2 group at p-position behaves in a different way than that of e-position.

(d) Hydrogen bonding exists in p-nitrophenol but no hydrogen bonding is present in o-nitrophenol.

[Hint: Intramolecular H-bonding is present in o-nitrophenol which lowers its boiling point while intermolecular Hbonding is present in p-nitrophenol which increases its boiling point.]

- 8. NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> are two forms of nitrogen dioxide. One exists in gaseous state while other in liquid state. The nature of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> forms are:
  - (a) both are paramagnetic
  - (b) both are diamagnetic
  - (c) NO<sub>2</sub> is paramagnetic while N<sub>2</sub>O<sub>4</sub> is diamagnetic
  - (d) NO<sub>2</sub> is diamagnetic while N<sub>2</sub>O<sub>4</sub> is paramagnetic

[Hint: NO2 is an odd electron molecule N

N<sub>2</sub>O<sub>4</sub>, has no unpaired electron.

$$N-N = 0$$

9. The formal charge of the O-atoms in

$$| : O = N = O : |$$
 is:

(a) -2

(c) 0

[Hint: Formal charge = total valence electrons in free atom - number of non-bonding electrons - 1/2 number of bonding electrons  $= 6 - 4 - 1/2 \times 4 = 0$ 

- 10. Among the following compounds the one that is polar and has the central atom with  $sp^2$  hybridization is :
  - (a) H<sub>2</sub>CO<sub>3</sub>
- (b) SiF<sub>4</sub>

(d) HClO<sub>2</sub>

[Hint:  $H_2CO_3$  is polar as  $H_2CO_3 \rightleftharpoons 2H^+ + CO_3^2$ . Carbon in  $CO_3^2$  ion is in  $sp^2$  hybridized state.]

11. Which of the following hydrocarbons has the lowest dipole moment?

(a) 
$$\stackrel{\text{CH}_3}{\text{H}} \searrow \text{C} = \text{C} \stackrel{\text{H}}{\swarrow} \text{CH}_3$$
 (b)  $\text{CH}_3\text{C} \equiv \text{CCH}_3$ 

(c)  $CH_3CH_2C = CH$ 

(d)  $CH_2 = CH - C = CH$ 

[Hint: Symmetrical with linear structure will have zero dipole moment.]

- 12. CO<sub>2</sub> is isostructural with:
  - (a) HgCl<sub>2</sub>
- (b) SnCl<sub>2</sub>

(c)  $C_2H_2$ 

(d) NO<sub>2</sub>

[Hint: The structure of CO<sub>2</sub> is linear O=C=O, similarly the structures of HgCl<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> are linear, Cl—Hg—Cl; HC=C-H. SnCl<sub>2</sub> and NO<sub>2</sub> have angular structures.]

- Which one of the following arrangements of molecules is correct on the basis of their dipole moments?
  - (a)  $BF_3 > NH_3 > NF_3$
- (b)  $BF_3 > NF_3 > NH_3$
- (c)  $NH_3 > BF_3 > NF_3$
- (d)  $NH_3 > NF_3 > BF_3$

[Hint: Both NF3 and NH3 have identical shape and a lone pair of electrons on nitrogen. The dipole moment of NH3 is higher than NF3 due to different directions of moments of the N—F and N—H bond. BF3 is a symmetrical molecule. It has zero dipole moment.

14. Lattice energy of BeCO<sub>3</sub> (I), MgCO<sub>3</sub> (II) and CaCO<sub>3</sub> (III) is in order:

(a) I < II < III

(b) I > II > III

(c) I < III < II

(d) II < I < III

[Hint: Lattice energy decreases with increase in size of the ions. The size of the cations  $Be^{2+} < Mg^{2+} < Ca^{2+}$ ]

15. Which of the following have undistorted octahedral structures?

1. SF<sub>6</sub>

2. PF<sub>6</sub>

3.  $SiF_6^{2-}$ 

4. XeF<sub>6</sub>

Select the correct answer using the codes given below:

(a) 2, 3 and 4

(b) 1, 3 and 4

(c) 1, 2 and 3

(d) 1, 2 and 4

**[Hint:** XeF<sub>6</sub> has distorted octahedral structure. Xenon in XeF<sub>6</sub> undergoes  $sp^3d^3$  hybridization giving pentagonal bipyramid with one axis is occupied by a lone pair.]

**16.** Sulphur reacts with chlorine in 1:2 ratio and forms *X*. Hydrolysis of *X* gives a sulphur compound *Y*. What is the hybridization state of central atom in the anion of *Y*?

(a)  $sp^3$ 

(b) sp

(c)  $sp^2$  (d)  $sp^2d$ 

[Hint:  $S + 2Cl_2 \longrightarrow SCl_4$ ;  $SCl_4 + 3H_2O \longrightarrow H_2SO_3 + 4HCl_4$ (X) (Y)

In  $SO_3^{2-}$ , sulphur has  $sp^3$  hybridization.]

17. Identify the correct sequence of increasing number of  $\pi$ -bonds in the structures of the following molecules :

(I) H<sub>2</sub>S<sub>2</sub>O<sub>6</sub>

(II) H<sub>2</sub>SO<sub>3</sub> (III) H<sub>2</sub>S<sub>2</sub>O<sub>5</sub>

(a) I, II, III

(b) II, III; I

(c) II, I, III

(d) I, III, II

List II

18. Match the following lists:
List I

Ethane 2 sp carbons (A) 1.  $6 sp^2$  carbons Ethylene  $2 sp^3$  carbons Acetylene  $2 sp^2$  carbons Benzene 1 sp and 1  $sp^2$  carbons The correct answer is: (A) (B) (C) (D) 3 4 2 (a) (b) 4 5 3 2 5 (c) 1 (d) 2

[Hint: Ethane  $H_3C$ — $CH_3$  ( $2sp^3$  carbons);  $sp^3 sp^3$ Ethylene  $H_2C$ = $CH_2$  ( $2sp^2$  carbons)  $sp^2 sp^2$ Acetylene HC=CH (2sp carbons) sp sp sp spBenzene  $sp^2 - C$   $sp^2 - C$   $sp^2$   $c - sp^2$   $c - sp^2$ 

19. The structure of diborane (B<sub>2</sub>H<sub>6</sub>) contains :

(a) four 2C-2e bonds and two 3C-2e bonds

 $(6 sp^2 carbons)$ 

(b) two 2C-2e bonds and four 3C-2e bonds

(c) two 2C-2e bonds and two 3C-2e bonds

(d) four 2C—2e bonds and four 3C—2e bonds

[Hint: The structure of B2H6 is:

Each boron atom is in  $sp^3$  hybrid state. Each boron has three orbitals associated with one electron each and one empty orbital. Two of orbitals to each boron atom overlap with hydrogen atoms (terminal) to form normal sigma bonds. Thus, four bonds are 2C-2e bonds.

Two hydrogen atoms overlap with rest of the four orbitals forming two 3C—2e bonds as two empty orbitals are involved.]

20. Molecular shapes of SF<sub>4</sub>, CF<sub>4</sub> and XeF<sub>4</sub> are :

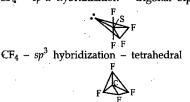
(a) the same with 2, 0 and 1 lone pair of electrons

(b) the same with 1, 1 and 1 lone pair of electrons

(c) different with 0, 1 and 2 lone pair of electrons

(d) different with 1, 0 and 2 lone pair of electrons [Hint: The structures are:

 $SF_4 - sp^3d$  hybridization – trigonal bipyramidal



 $XeF_4 - sp^3d^2$  hybridization – octahedral



21. Which of the following is correct?

(a) The number of electrons present in the valence shell in SF<sub>6</sub> is 12.

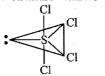
(b) The rates of ionic compounds are very slow.

(c) According to VSEPR, SnCl2 is a linear molecule.

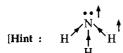
(d) The correct order of ability to form ionic compounds among  $Na^+$ ,  $Mg^{2+}$  and  $Al^{3+}$  is  $Al^{3+} > Mg^{2+} > Na^+$ .

- 22. Which of the following is not isostructural with SiCl<sub>4</sub>?
  - (a)  $PO_4^{3}$
- (b) NH<sub>4</sub><sup>+</sup>
- (c) SCl<sub>4</sub>
- (d) SO<sub>4</sub><sup>2</sup>

[Hint: S in SCl<sub>4</sub> undergoes  $sp^3d$  hybridization. Thus, the molecule has see-saw structure whereas SiCl<sub>4</sub> is tetrahedral.



- 23. The electronegativity difference between N and F is greater than that between N and H, yet the dipole moment of  $NH_3(1.5 D)$  is larger than that of  $NF_3(0.2 D)$ . This is because:
  - (a) in NH<sub>3</sub> as well as in NF<sub>3</sub>, the atomic dipole and bond dipole are in opposite directions
  - (b) in NH<sub>3</sub>, the atomic dipole and bond dipole are in the opposite directions whereas in NF3, these are in the
  - (c) in NH<sub>3</sub> as well as in NF<sub>3</sub>, the atomic dipole and bond dipole are in the same direction
  - (d) in NH<sub>3</sub>, the atomic dipole and bond dipole are in the same direction whereas in NF3, these are in the opposite directions





- 24. In which of the following molecules are all the bonds not equal?
  - (a) AlF<sub>3</sub>

(b) NF<sub>3</sub>

(c) ClF<sub>3</sub>

(d) BF<sub>2</sub>

[Hint: Cl in CIF<sub>3</sub> is in  $sp^3d$  hybridization. The molecule has T-shape structure.]



- Which of the following is not a correct statement?
  - (a) Every AB<sub>5</sub> molecule does in fact have square pyramidal structure.
  - (b) Multiple bonds are always shorter than corresponding single bonds.
  - (c) The electron deficient molecules act as Lewis acids.
  - (d) The canonical structures have no real existence.

[Hint: AB5 molecule can be either square pyramidal as IF5 or trigonal bipyramid as PCl<sub>5</sub>.]

- Specify the coordination geometry around and hybridization of N and B atoms in the 1:1 complex of BF<sub>3</sub> and NH<sub>3</sub>:
  - (a) N: tetrahedral, sp<sup>3</sup>, B: tetrahedral, sp<sup>3</sup>
  - (b) N: pyramidal, sp<sup>3</sup>, B: pyramidal, sp<sup>3</sup>
  - (c) N: pyramidal, sp3, B: planar, sp2
  - (d) N: pyramidal,  $sp^3$ , B: tetrahedral,  $sp^3$

[Hint: The lone pair present on nitrogen in ammonia molecule is donated to boron as BF3 is an electron deficient molecule forming a coordinate bond.



Both N and B are in sp3-hybrid state, i.e., two tetrahedral are joined with each other.]

- 27. Identify the correct order of decreasing bond strength in the bonds formed by 2s-2s, 2p-2p and 2s-2p overlapping:
  - (a) 2s-2s > 2s-2p > 2p-2p
- (b) 2s-2s > 2p-2p > 2s-2p
- (c) 2p-2p > 2s-2p > 2s-2s
- (d) 2p-2p > 2s-2s > 2s-2p

[Hint: Bond strength depends on the extent of overlapping. Maximum overlapping occurs in the case of p-orbitals.]

- The hybridization of I in ICl<sub>2</sub> is:
  - (a) sp

(b)  $sp^2$ 

- (c)  $sp^3$
- (d)  $dsp^2$

[Hint: State of hybridization, H = 1/2[7 + 2 - 1 + 0] = 4or sp<sup>3</sup>-hybridized]

- 1. (d) 2. (d) **11.** (b) **12.** (a,c)
- 3. (a)
- 4. (b)
- 5. (c)
- 6. (b)
- 7. (a)
- 8. (c)
- 9. (c)
- 10. (a)

- 13. (d)
- 14. (b)
- 15. (c)
- 16. (a)
- 17. (b)
- 18. (a)

28. (c)

- **22.** (c)
- 23. (d)

- 25. (a)
- 26. (a)
- 27. (c)
- 19. (a)
- 20. (d)

- 21. (a)

# Matrix Matching Questions for IIT Aspirants

Match List-I with List-II:

List-I

List-II

- (a) Molecule with sp hybrid
- (p) H-C=C-H

carbon

- (b) Allene (q)  $CH_2 = C = CH_2$
- (c) Electron deficient
- (r) PCl<sub>5</sub>
- (d) Expanded octet
- (s) BeCl<sub>2</sub>
- 2. Match List-I with List-II:

List-I

List-II

- (a) PCl<sub>5</sub>
- (p) Two axial bonds + three lone pairs
- (b) XeF<sub>2</sub>
- (q) Two axial + two equitorial bonds
- (c) SF<sub>4</sub>
- (r) Two axial + one equitorial bonds
- (d) CIF<sub>3</sub>
- (s) Three equitorial + two axial bonds
- Match the molecular species in List-I with their shape in

List-I

List-II

- (a) Linear shape
- (p) CS<sub>2</sub>
- (b) sp hybridization
- (q) XeF<sub>2</sub>
- (c)  $sp^3d$  hybridization
- (r)  $C_2H_2$
- (d) CO2 is isostructural to
- (s) NCO

(c)  $sp^{3}d^{3}$ 

List-I and shape in List-III:

- List-III
- (p)  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ 
  - (q)  $d_{x^2-y^2}$ ,  $d_{z^2}$

4. Match the orbitals in List-II with the hybridization in

- (u) Octahedral (v) Pentagonal
- - bipyramidal
- (r) d<sub>7</sub>2 (w) Trigonal

bipyramidal

5. Match the molecular species in List-I and their magnetic and molecular orbital properties in List-II:

List-I

List-I

(a)  $sp^3d$ 

(b)  $sv^3d^2$ 

List-II (p) Bond order = 2

(a)  $O_2$ 

(b)  $N_2$ 

(q) Diamagnetic

(c) H<sub>2</sub> (d)  $O_2^{2-}$ 

- (r) Bond order = 3
- (s) Paramagnetic

(a-q, r, p, s)

- (a-p, q) (a-s)
- (b-q) (b-p)

(b-p, r, s)

(c-s)

(c-q)

- (d-r)(d-r)(d-p)
- (c-q)

- (b-q-u)
- (c-p-v)
- (a-r-w) (a-p, s)
- (b-q, r)
- (d-q) (c-q)

# **Assertion-Reason Type Questions**

The questions given below consist of an Assertion (A) and **Reason (R).** Use the following key to choose the correct answer.

- (a) If both (A) and (R) are correct and (R) is the correct explanation of the (A).
- (b) If both (A) and (R) are correct but (R) is not the correct explanation of the (A).
- (c) If (A) is correct but (R) is incorrect.
- (d) If both (A) and (R) are incorrect.
- 1. (A) Bond order in a molecule can assume any value, positive or negative, integral or fractional including zero.
  - (R) It depends upon the number of electrons in the bonding and antibonding orbitals. [A.I.LM.S. 1994]
- 2. (A) Ionic compounds tend to be non-volatile.
  - (R) Intermolecular forces in these compounds are weak. [A.I.LM.S. 1994]
- 3. (A) The atoms in a covalent molecule are said to share electrons, yet some covalent molecules are polar.
  - (R) In polar covalent molecule, the shared electrons spend more time on the average near one of the atoms.
    - [A.I.I.M.S. 1996]

- 4. (A) Nitrogen is inreactive at room temperature but becomes reactive at elevated temperature (on heating or in the presence of catalysts).
  - (R) In nitrogen molecule, there is extensive delocalization of electrons. [A.I.I.M.S. 1996]
- 5. (A) Water is a good solvent for ionic compounds but poor one for covalent compounds.
  - (R) Hydration energy of ions releases sufficient energy to overcome lattice energy and break hydrogen bonds in water while covalent bonded compounds interact so weakly that even van der Waals' forces between molecules of covalent compounds cannot be broken.

[A.I.I.M.S. 1996]

- 6. (A) Na<sub>2</sub>SO<sub>4</sub> is soluble in water while BaSO<sub>4</sub> is insoluble.
  - (R) Lattice energy of BaSO<sub>4</sub> exceeds its hydration energy. [A.I.I.M.S. 1997]
- 7. (A) NO<sub>3</sub> is planar while NH<sub>3</sub> is pyramidal.
  - (R) N in  $NO_3$  is  $sp^2$  and in  $NH_3$  it is  $sp^3$  hybridized.

[A.I.I.M.S. 1997]

- 8. (A) N<sub>2</sub> and NO<sup>+</sup> both are diamagnetic substances.
  - (R) NO<sup>+</sup> is isoelectronic with N<sub>2</sub>.

[A.I.I.M.S. 1997]

- 9. (A) The bond angle of PBr<sub>3</sub> is greater than PH<sub>3</sub> but the bond angle of NBr<sub>3</sub> is less than NH<sub>3</sub>.
   (R) Electronegativity of phosphorus atom is less than that
  - (R) Electronegativity of phosphorus atom is less than that of nitrogen. [A.I.I.M.S. 1997]
- 10. (A) The electronic structure of  $O_3$  is



(R) Structure is not allowed because octet around

'O' cannot be expanded.

[I.I.T. 1998]

- 11. (A) LiCl is predominantly a covalent compound.
  - (R) Electronegativity difference between 'Li' and 'Cl' is too small. [I.I.T. 1998]
- 12. (A) Bond order can assume any value including zero.
  - (R) Higher the bond order, shorter is the bond length and greater is the bond energy. [A.I.I.M.S. 1999]

- 13. (A) The dipole moment helps to predict whether molecule is polar or non-polar.
  - (R) The dipole moment helps to predict the geometry of molecules. [A.I.I.M.S. 1999]
- 14. (A) The O—O bond length in H<sub>2</sub>O<sub>2</sub> is shorter than that of O<sub>2</sub>F<sub>2</sub>.
  - (R)  $H_2O_2$  is an ionic compound.

[A.I.I.M.S. 2003]

- 15. (A) All F—S—F angles in SF<sub>4</sub> are greater than 90° but less than 180°.
  - (R) The lone pair-bond repulsion is weaker than bond pair-bond repulsion. [A.I.I.M.S. 2004]
- 16. (A) B<sub>2</sub> molecule is diamagnetic.
  - (R) The highest occupied molecular orbital is of  $\sigma$  type. [Hint: In B<sub>2</sub>, total number of electrons are  $10 \ (\sigma 1s)^2 (\mathring{\sigma} 1s)^2 \ (\sigma 2s)^2 (\mathring{\sigma} 2s)^2 (\pi 2p_y)^1 (\pi 2p_z)^1$ -paramagnetic. The highest occupied orbital is of  $\pi$  type.]
- 17. (A) The S—S—S bond angle in S<sub>8</sub> molecule is 105°.
  - (R) S<sub>8</sub> has V-shape.

[A.I.I.M.S. 2008]

- 18. (A) Fluorine molecule has bond order one.
  - (R) The number of electrons in antibonding molecular orbitals is two less than in bonding molecular orbitals.

    [A.I.I.M.S. 2008]

# Auswers

1. (a) 2. (c) 4. (c) 5. (a) 3. (a) 6. (a) 7. (a) 8. (a) 9. (b) 10. (b) 11. (c) 12. (b) 13. (a) 14. (d) 15. (c) 16. (d) 17. (c) 18. (a)

# **THOUGHT TYPE QUESTIONS**

# THOUGHT 1

When anions and cations approach each other, the valence shell of anions are pulled towards cation nucleus and thus, shape of anion is deformed. The phenomenon of deformation of anion by a cation is known as polarization and the ability of the cation to polarize the anion is called as polarizing power of cation. Due to polarization, sharing of electrons occurs between two ions to some extent and the bond shows some covalent character.

The magnitude of polarization depends upon a number of factors. These factors were suggested by Fajan and are known as Fajan's rules.

- (i) Greater is the polarization in a molecule, more is covalent character.
- (ii) As the charge on cation increases, its tendency to polarize the anion increases.
- (iii) As the size of the cation decreases or size of the anion increases, the polarization increases.
- (iv) The cations with 18 electrons in the outermost shell bring greater polarization of the anion than those with inert gas configuration even both the cations have same size and same charge.

- Considering BeCl<sub>2</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub> and BaCl<sub>2</sub>, predict which
  of the following statements is true?
  - (a) BeCl<sub>2</sub> is least ionic out of the given chlorides
  - (b) Covalent character increases as the atomic number of the metal atom increases
  - (c) BeCl<sub>2</sub> has the highest melting point among the given chlorides
  - (d) All are highly ionic compounds
- 2. In which of the halides, there is maximum polarization?
  - (a) AlF<sub>3</sub>
- (b) AlCl<sub>3</sub>
- (c) AlBr<sub>3</sub>
- (d) AlI<sub>3</sub>
- 3. Which is most covalent in nature?
  - (a) NaCl
- ( MgCl<sub>2</sub>

- (c) AICL
- (d) CaCl<sub>2</sub>
- 4. Non-aqueous solvent like ether is added to the mixture of LiCl, NaCl and KCl. Which will be extracted into ether?
  - (a) NaCl
- (b) LiCl

(c) KC1

- (d) None
- 5. Which has the minimum melting point?
  - (a) CaF<sub>2</sub>
- (b) CaCl<sub>2</sub>
- (c) CaBr<sub>2</sub>
- (d) CaI<sub>2</sub>

#### THOUGHT 2

Covalent molecules formed by heteroatoms bound to have some ionic character. The ionic character is due to shifting of the electron pair towards A or B in the molecule AB. Hence, atoms acquire small and equal charge but opposite in sign. Such a bond which has some ionic character is described as polar covalent bond. Polar covalent molecules can exhibit dipole moment. Dipole moment is equal to the product of charge separation, q and the bond length, d for the bond. The unit of dipole moment is Debye. One Debye is equal to  $10^{-18}$  esu cm.

Dipole moment is a vector quantity. It has both magnitude and direction. Hence, dipole moment of molecules depends upon the relative orientation of the bond dipoles, but not on the polarity of bonds alone. A symmetrical structure shows zero dipole moment. Thus, dipole moments help to predict the geometry of the molecules. Dipole moment values can be used to distinguish between *cis*- and *trans*-isomers; *ortho-*, *meta-* and *para-*forms of a substance, etc. The percentage of ionic character of a bond can be calculated by the application of the following formula:

#### % ionic character

1. Which of the following compounds have zero dipole moments?

[Hint: Symmetrical forms have zero dipole moments.]

2. Which are non-polar molecules?

(a) XeF<sub>4</sub>

(b) BF<sub>3</sub>

(c) NH<sub>3</sub>

(d) H<sub>2</sub>O

3. A diatomic molecule has a dipole moment of 1.2 D. If the bond length is  $1.0 \times 10^{-8}$  cm, what fraction of charge does exist on each atom?

(a) 0.1

(b) 0.2

(c) 0.25

(d) 0.3

[Hint : Charge =  $\frac{\text{Dipole moment}}{\text{Bond length}} = \frac{1.2 \times 10^{-18}}{1.0 \times 10^{-8}} = 1.2 \times 10^{-10} \text{esu}$ 

Fraction of electronic charge =  $\frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}}$  = 0.25]

**4.** Arrange the following compounds in increasing order of dipole moments, toluene (I), *o*-dichlorobenzene (II),

m-dichlorobenzene (III) and p-dichlorobenzene (IV):

(a) IV < I < II < III

(b) I < IV < II < III

(c) IV < I < III < II

(d) IV < II < I < III

- 5. The dipole moment of NF<sub>3</sub> is very much less that of NH<sub>3</sub> because :
  - (a) number of lone pairs in NF<sub>3</sub> is much greater than in NH<sub>3</sub>
  - (b) unshared electron pair is not present in NF3 as in NH3
  - (c) both have different shapes
  - (d) of different directions of moments of N—H and N—F bonds
- 6. A covalent molecule, x-y, is found to have a dipole moment of  $1.5 \times 10^{-29}$  cm and a bond length 150 pm. The percentage of ionic character of the bond will be:

(a) 50%

(b) 62.5%

and the second second second second second second second second second second second second second second second

(c) 75% (d) 90%

[**Hint**:  $\mu_{cal} = 1.602 \times 10^{-19} \text{C} \times 150 \times 10^{-12} \text{ m} = 2.4 \times 10^{-29} \text{ cm}$   $\mu_{obs} = 1.5 \times 10^{-29}$ % ionic character  $= \frac{1.5 \times 10^{-29}}{2.4 \times 10^{-29}} \times 100 = 62.5$  ]

#### THOUGHT 3

According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with almost same energy and similar positions of nuclei, bonding and non-bonding pairs of electrons are taken as canonical structures of the resonance hybrid which describes the molecule accurately. In general, the resonance stabilizes the molecule as the energy of resonance hybrid is less than the energy of any single canonical structure and resonance averages the bond characteristics as a whole. Actually resonance hybrid does not oscillate between the canonical forms but it is a definite form and has a definite structure which cannot be written on paper. The contributing structures should be such that negative charge resides on more electronegative and positive charge on the electropositive. Like charges should not reside on atoms close together in the canonical forms.

As a result of resonance, the bond order changes in many molecules or ions.

Total number of bonds between two atoms in all the structures

Total number of resonating structures

Formal charges on atoms in the molecule helps in selecting most favourable canonical form to the hybrid form.

 Consider the following statements about the resonating structures of benzene.

$$\underbrace{\bigcirc \longleftrightarrow \bigcirc \longleftrightarrow \bigcirc \longleftrightarrow \bigcirc \longleftrightarrow \bigcirc \longleftrightarrow \bigcirc
}_{\text{Kekule's}}$$

$$\underbrace{\bigcirc \longleftrightarrow \bigcirc \longleftrightarrow \bigcirc \longleftrightarrow \bigcirc
}_{\text{Dewar's}}$$

The correct statement(s) is/are:

(a) Two Kekule's structures contribute 80% while remaining three Dewar's structures 20% only.

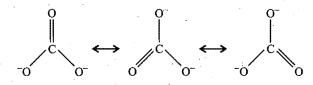
- (b) Because of the resonance, all C—C bonds in benzene become identical.
- (c) Resonance decreases the bond length of C—C single bond and increases the bond length of C=C bond.
- (d) Benzene becomes less stable and more reactive due to resonance.
- 2. The bond order of C—O bond for  $CO_3^{2-}$  ion is:
  - (a) 1.25

(b) 1.33

(c) 1.5

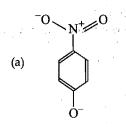
(d) 1.0

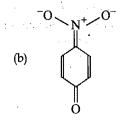
[Hint: The resonance structures of carbonate ion are:

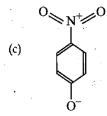


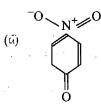
B.O. = 
$$\frac{2+1+1}{3}$$
 = 1.33]

- 3. Which is not true for resonance?
  - (a) Identical bonding
  - (b) Identical arrangement of atoms
  - (c) Same number of paired electrons
  - (d) Structure with nearly same energies
- **4.** The most unlikely representation of resonance structure of *p*-nitrophenoxide ion is:









- 5. Which resonance structure of  $N_2O$  is more favourable than others?
  - (a)  $\vec{N} = \vec{N} = \vec{O}$
- (b)  $: N = \stackrel{+}{N} O$ :
- (c)  $^{2-}$ : $\overset{+}{N} = \overset{+}{O}$ :
- (d) None

[Hint: Negative charge should be present on more electronegative atom.]

#### **THOUGHT 4**

Molecular orbital theory is based on the principle of linear combination of atomic orbitals. According to this approach when atomic orbitals of the atoms come closer, they undergo constructive interference as well as destructive interference giving molecular orbitals, *i.e.*, two atomic orbitals overlap to form two molecular orbitals, one of which lies at a lower energy level (bonding molecular orbital) than the other at higher energy level (antibonding molecular orbital). Each molecular orbital can hold one or two electrons in accordance with Pauli's exclusion principle and Hund's rule of maximum multiplicity. For molecules upto  $N_2$ , the order of filling of orbitals is:

$$\sigma(1s)$$
,  $\mathring{\sigma}(1s)$ ,  $\sigma(2s)$ ,  $\mathring{\sigma}(2s)$ ,  $\pi(2p_x) = \pi(2p_y)$ ,  $\sigma(2p_z)$ ,  $\mathring{\pi}(2p_x) = \mathring{\pi}(2p_y)$ ,  $\mathring{\sigma}(2p_z)$ 

and for molecules after  $N_2$ , the order of filling is:

$$\sigma(1s), \ \mathring{\sigma}(1s), \ \sigma(2s), \ \sigma(2s), \ \sigma(2p_z), \ \pi(2p_x) = \pi(2p_y), \ \mathring{\pi}(2p_x) = \mathring{\pi}(2p_y), \ \mathring{\sigma}(2p_z)$$

Bond order =  $\frac{1}{2}$  [bonding electrons – antibonding electrons]

Bond order gives the following information:

- (i) If bond order is greater than zero, the molecule/ion exists otherwise not.
- (ii) Higher the bond order, higher is the bond dissociation energy.
- (iii) Higher the bond order, greater is the bond stability.
- (iv) Higher the bond order, shorter is the bond length.
- **1.** The relative stabilities of CN, CN<sup>+</sup> and CN<sup>-</sup> are in the order of :
  - (a)  $CN > CN^{+} > CN^{-}$
- (b) CN7 > CN > CN+
- (c)  $CN^- > CN^+ > CN$
- (d)  $CN^+ > CN > CN^-$

[**Hint**: Bond order:  $CN = \frac{9-4}{2} = 2.5$ ,  $CN^- = \frac{10-4}{2} = 3$ ,  $CN^+ = \frac{8-4}{2} = 2$ ]

- 2. Molecular orbital theory is preferred over valence bond theory as it can explain:
  - (a) bond strength
  - (b) geometry of molecule
  - (c) the magnetic nature of the molecule
  - (d) none of the above
- 3.  $O_2^2$  will have:
  - (a) bond order lower than O2
  - (b) bond order higher than O2
  - (c) bond order equal to O2
  - (d) bond order equal to H2
- 4. Which of the following molecule is paramagnetic?
  - (a) F<sub>2</sub>

(b) O<sub>2</sub>

(c)  $N_2$ 

- (d) H<sub>2</sub>
- 5. In which set of molecules all the species are paramagnetic?
  - (a)  $B_2$ ,  $O_2$ ,  $N_2$
- (b) B<sub>2</sub>, O<sub>2</sub>, NO
- (c)  $B_2$ ,  $F_2$ ,  $O_2$
- (d) B<sub>2</sub>, O<sub>2</sub>, Li<sub>2</sub>
- 6. Which one of the following statements is correct?
  - (a) Bonding molecular orbital is lowered by the same, amount of energy by which antibonding molecular orbital is raised.
  - (b) Bonding molecular orbital is lowered by greater amount of energy than the amount by which antibonding molecular orbital is raised.

- (c) Bonding molecular orbital is lowered by lesser amount of energy than the amount by which antibonding molecular orbital is raised.
- (d) Any one of the above is possible.

# Auswers

Thought 1	1. (a)	2. (d)	3. (c)	4. (b)	5. (d)	
Thought 2	1. (b,d)	2. (a,b)	3. (c)	4. (c)	5. (d)	<b>6.</b> (b)
Thought 3	1. (a,b,c)	2. (b)	3. (a)	<b>4.</b> (c)	5. (b)	*
Thought 4	1. (d)	2. (c)	3. (a,d)	4. (b)	5. (b)	6. (c)

# INTEGER ANSWER Tupe Objections

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. What is the % ionic character in HI? Given electronegativity of H = 2 and I = 2.5.
- 2. The number of orbitals involved in the hybridisation of XeF<sub>2</sub> is :
- 3. The formal charge on the carbon atom in the carbonate ion is:
- 4. In SF<sub>4</sub>, S atom has  $dsp^x$  hybridisation. What is the value of
- 5. How many total bonds (sigma and pi bonds) are present in ozone molecule?
- 6. A complex ion [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is found to be paramagnetic. Its magnetic moment is 4.89 BM. How many unpaired electrons are present?

- 7. Dipole moment of certain diatomic molecule X—Y is 0.38 D. If the X—Y distance is 158 pm, the percentage of electronic charge developed on X-atom is:
- 8. How many electrons are present in antibonding MO's in CN<sup>+</sup> ion?
- **9.** How many carbon atoms of 1,3-butadiene have  $sp^2$ -hybrid state?
- 10. The number of pi bonds present in tetracyanoethylene molecule is:
- 11. The number of lone pairs on Xe in XeF<sub>6</sub> is:
- 12. The maximum number of hydrogen bonds that a molecule of water can have is:

# Auswers

- 1. (7) Percentage ionic character =  $[16(X_A X_B) + 3.5 (X_A X_B)^2]$ =  $16 \times 0.4 + 3.5 \times (0.4)^2 = 7$
- 2. (5) H = 1/2 [V + M C + A]

where H = Number of orbitals involved in hybridisation

V = Valence electrons of central atom

M = Number of monovalent atoms linked with central atom

C = Charge on the cation

A = Charge on the anion

H = 1/2[8 + 2 - 0 + 0] = 5

(0) Formal charge = Valence electrons - lone pair electrons
 1/2 bonding electrons

$$O = 4 - 0 - 1/2 \times 8 = 0$$

$$C \qquad C$$

4. (3) 
$$H = 1/2 [V + M - C + A]$$
  
= Number of orbitals involved  
=  $1/2 [6 + 4 - 0 + 0] = 5$   
 $dsp^{x} = 1 + 1 + 3 = 5$ 

- 5. (3) 2 sigma and one pi bonds
- 6. (4) Magnetic moment =  $\sqrt{n(n+2)}$  = 4.89 BM =  $\sqrt{4 \times 6}$  = 4.89 BM

7. (5) 
$$\delta^+ = \frac{\mu_{xy}}{d_{x-y}} = \frac{0.38 \times 10^{-18}}{158 \times 10^{-10}} = 2.4 \times 10^{-11}$$
  
% electron charge  $= \frac{2.4 \times 10^{-11}}{4.8 \times 10^{-10}} \times 100 = 5$ 

- 8. (4) Configuration of CN<sup>+</sup> ion is  $KK(\sigma 2s)^2(\sigma 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2$
- 9. (4)  $CH_2 = CH CH = CH_2$

All the carbon atoms are  $sp^2$  hybridised.

10. (9) The structure of tetracyanoethylene is :

- 11. (1) XeF<sub>6</sub>
  The molecule has pentagonal bipyramidal geometry with one apex occupied by a lone pair.
- 12. (4)



#### Contents:

- 3.1 Introduction
- 3.2 Arrhenius Concept
- 3.3 Bronsted-Lowry Concept
- 3.4 Lewis Concept
- 3.5 The Lux-Flood Concept
- 3.6 Usanovich Concept
- 3.7 Hard and Soft Acids and Bases
- 3.8 Some General Trends in Acidic and Basic Properties

# 3.1 INTRODUCTION

Acids and bases were first recognised as specific classes of compounds because of the distinctive properties exhibited by their aqueous solutions. The properties of acids and bases are listed below:

Properties of acids	Properties of bases
1. Sour* in taste.	Bitterness in taste.
2. Change colours of indicators,	Change colours of indicators, e.g.,
e.g., litmus turns from blue to	litmus turns from red to blue;
red; phenolphthalein turns	phenolphthalein turns from
from pink to colourless.	colourless to pink.
3. Electrolytic conductivity in aqueous solution.	l
4. React with active metals to give hydrogen.	Soapy touch and slippery in nature.
	Basic properties disappear when react with acids (Neutralisation).
6. Decompose carbonates.	

In 1783, **Lavoisier** suggested that acids are the oxy-compounds of non-metals. This view was soon rejected by Davy as a result of his studies on *muriatic acid* (hydrochloric acid). The search for a common factor in acids came to light when the German chemist, **Liebig**, proposed the following definition of an acid in 1830.

# CHAPTER 3

# Acids and Bases

An acid is a compound which contains one or more hydrogen atoms replaceable partially or completely by a metal or a positive radical to produce a salt.

Several theories (concepts) have been proposed to explain the behaviour of acids and bases on the basis of structure and composition, but no single theory explains the overall behaviour of acids and bases. Each of the theory or concept can be applied with advantage in appropriate circumstances. In a given situation, the chemist uses that concept which best suits his purpose.

The most popular theories or concepts are described in this chapter.

### 3.2 ARRHENIUS CONCEPT

This concept was presented in 1887. According to this concept all substances which give H<sup>+</sup> ions when dissolved in water are called acids while those which ionise in water to furnish OH<sup>-</sup> ions are called bases.

$$HA \stackrel{\text{Water}}{=\!=\!=\!=} H^+ + A^-$$
Acids 
$$BOH \stackrel{\text{Water}}{=\!=\!=\!=} B^+ + OH^-$$
Base

Warning: The chemicals in the laboratory should never be tasted as these can be poisonous and prove fatal sometimes.

<sup>\*</sup> The word acid is a Latin word—acidus meaning sour.

The reaction between an acid and a base is termed neutralisation, *i.e.*, neutralisation involves the reaction between H<sup>+</sup> and OH<sup>-</sup> ions to form water.

$$NaOH + HCI \longrightarrow NaCI + H_2O$$
 (Neutralisation)  
Base Acid Salt Water  $OH^- + H^+ \longrightarrow H_2O$ 

Actually free  $H^+$  ions do not exist in water. They combine with solvent molecules, *i.e.*, hydrated to form **hydronium** or **hydroxinium** ( $H_3O^+$ ) ions.

$$H^+ + H_2O \Longrightarrow H_3O^+(aq)$$

Thus, the ionisation of acids in aqueous solutions should be represented as:

$$HCl + H_2O \Longrightarrow H_3O^+(aq) + C\Gamma(aq)$$
  
 $H_2SO_4 + 2H_2O \Longrightarrow 2H_3O^+(aq) + SO_4^{2-}(aq)$ 

Evidence for Arrhenius theory comes from the heat of reaction,  $\Delta H^{\circ}$ , for the neutralisation of a strong acid by a strong base. This neutralisation is essentially the reaction of  $H_3O^+(aq)$  with  $OH^-(aq)$  and should, therefore, always give the same  $\Delta H^{\circ}$  per mole of water formed. Experimentally, it is found that all neutralisation between strong acids and strong bases have the same  $\Delta H^{\circ}$  (–55.90 kJ per mole of  $H^+$ ).

#### Limitations of Arrhenius Concept

- (i) It is applicable only to aqueous solutions. For the acidic or basic properties, the presence of water is absolutely necessary. Dry HCl shall not act as an acid.
- (ii) The concept does not explain acidic or basic properties of acids and bases in non-aqueous solvents respectively.
- (iii) It fails to explain the acidic nature of the non-protic compounds such as  $SO_2$ ,  $NO_2$ ,  $CO_2$ ,  $P_2O_5$ , etc., which do not have hydrogen for furnishing  $H^+$  ions.
- (iv) It fails to explain the basic nature of compounds like NH<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, etc., which do not have OH in the molecule to furnish OH<sup>-</sup> ions.
- (v) It fails to explain the acidic nature of certain salts such as  $AlCl_3$  in aqueous solution.

#### Modified Arrhenius Concept

The modified concept rectifies most of the limitations. Water is a weak electrolyte and ionises to a very small extent.

$$\frac{H_2O \Longrightarrow H^+ + OH^-}{H^+ + H_2O \Longrightarrow H_3O^+}$$

$$\frac{H^+ + H_2O \Longrightarrow H_3O^+ + OH^-}{H_2O + H_2O \Longrightarrow H_3O^+ + OH^-}$$

Water is also neutral in nature, *i.e.*,  $H_3O^+$  and  $OH^-$  ion concentrations are equal.

$$[H_3O^+] = [OH^-]$$

The substances which increase the concentration of  $H_3O^+$  ions in water act as acids while those which increase the concentration of  $OH^-$  ions act as bases.  $SO_2$  increases  $H_3O^+$  ion concentration. Hence, it is an acid.

$$SO_2 + H_2O \longrightarrow H_2SO_3 \stackrel{Water}{\Longleftrightarrow} H_3O^+ + HSO_3^-$$

Similarly, NH<sub>3</sub> behaves as a base as it increases OH<sup>-</sup> ion concentration.

$$NH_3 + H_2O \longrightarrow NH_4OH \Longrightarrow NH_4^+ + OH^-$$

#### Basicity or Protocity of an Acid

The basicity of an acid is the number of hydrogen ions which can be furnished by one molecule of the acid upon dissociation. An acid liberating 1, 2 or 3 H<sup>+</sup> ions are respectively known as monobasic, dibasic and tribasic (monoprotic, diprotic and triprotic). Polyprotic acids usually dissociate in steps.

Acid	Dissociation	Basicity
HCI	HCl <del>←</del> H <sup>+</sup> + Cl <sup>-</sup>	1 [Monoprotic]
HNO <sub>3</sub>	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	1 [Monoprotic]
CH <sub>3</sub> COOH	CH <sub>3</sub> COOH ⇌ H <sup>+</sup> + CH <sub>3</sub> COO <sup>-</sup>	1 [Monoprotic]
H <sub>2</sub> SO <sub>4</sub>	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ $HSO_4^- \rightleftharpoons H^+ + SO_4^{2}$	
	$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$	2 [Diprotic]
H <sub>3</sub> PO <sub>4</sub>	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	
*	$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2^-}$ $HPO_4^{2^-} \rightleftharpoons H^+ + PO_4^{3^-}$	
	$H_3PO_4 \Longrightarrow 3H^+ + PO_4^{3-}$	3 [Triprotic]
$H_3PO_3$	$H_3PO_3 \Longrightarrow H^+ + H_2PO_3^-$	
r J	$H_2PO_3^- \iff H^+ + HPO_3^{2-}$	of the second
	$H_3PO_3 \iff 2H^+ + HPO_3^{2-}$	2 [Diprotic]
H <sub>3</sub> PO <sub>2</sub>	$H_3PO_2 \iff H^+ + H_2PO_2^-$	1 [Monoprotic]

It is clear from the above table that basicity of an acid is not necessarily the number of hydrogen atoms present in one molecule of the acid but the number of hydrogen ions furnished by one molecule. An acid is generally termed as **polybasic** or **polyprotic** when a molecule of it produces more than one  $H^+$  ion in aqueous solution.

#### Acidity or Hydroxicity of a Base

The acidity or hydroxicity of a base is the number of hydroxyl ions produced from one molecule of the base on dissociation. A base liberating 1, 2 or 3 OH<sup>-</sup> ions are respectively known as monoacidic or monohydroxic, diacidic or dihydroxic, triacidic or trihydroxic. Sodium hydroxide (NaOH), ammonium hydroxide (NH<sub>4</sub>OH), potassium hydroxide (KOH) are monoacidic or monohydroxic bases while calcium hydroxide [Ca(OH)<sub>2</sub>], barium hydroxide [Ba(OH)<sub>2</sub>] are diacidic or dihydroxic bases.

[Acidity may also be considered as the number of H<sup>+</sup> ions that can be accepted by one molecule of the base.]

#### Strength of Acids and Bases

The strength of an acid or a base in Arrhenius concept is based on the extent of ionisation or the equilibrium constant. The equilibrium constant,  $K_a$  for the acid, HX, is:

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

The equilibrium constant,  $K_b$  for the acid, BOH, is:

$$K_b = \frac{[B^+][\mathrm{OH}^-]}{[B\mathrm{OH}]}$$

The acids which are highly ionised in aqueous solutions, *i.e.*, giving large number of hydrogen ions are known as strong acids. The value of  $K_a$  for strong acids is higher than 0.1. HClO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, etc., are very strong acids. The value of  $K_a$  is very small for weak acids such as CH<sub>3</sub>COOH, H<sub>3</sub>PO<sub>3</sub>, H<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, etc. For example,  $K_a$  value of CH<sub>3</sub>COOH is 1.8 × 10<sup>-5</sup> at 25°C. In other words, in the case of weak acid, the ionisation is only slight and the major part remains as undissociated molecules.

The bases which are highly dissociated in aqueous solution to produce large number of  $OH^-$  ions are called strong alkalies. The value of  $K_b$  for strong alkalies is higher than 0.1. NaOH, KOH, Ba(OH)<sub>2</sub>, etc., are strong bases. The value of  $K_b$  is low for weak bases such as  $NH_4OH$ ,  $Al(OH)_3$ ,  $Fe(OH)_3$ , etc.

### 3.3 BRONSTED-LOWRY CONCEPT

The concept was proposed independently by Bronsted and Lowry in 1923. According to this concept acids are the species capable of donating the proton in a reaction while bases are the species capable of accepting the proton in a reaction, *i.e.*, acids are proton donors (protogenic) and bases are proton acceptors (protophilic). Consider the reaction,

$$HC1 + H_2O \Longrightarrow H_3O^+ + C1^-$$

In this reaction, HCl acts as an acid because it donates a proton to the water molecule. Water, on the other hand, behaves as a base by accepting a proton from an acid. Some other examples are:

$$CH_3COOH + H_2O \Longrightarrow H_3O^+ + CH_3COO^-$$
  
 $CO_2 + 2H_2O \Longrightarrow H_3O^+ + HCO_3^-$   
 $NH_4^+ + H_2O \Longrightarrow H_3O^+ + NH_3$   
 $HSO_4^- + H_2O \Longrightarrow H_3O^+ + SO_4^{2-}$ 

Consider the reaction,

$$NH_3 + H_2O \Longrightarrow NH_4^+ + OH^-$$

In this reaction, water acts as an acid as it donates a proton to  $NH_3$  molecule and  $NH_3$  behaves as a base as it accepts a proton. Some other examples are :

$$OH^- + H^+ \Longrightarrow H_2O$$
  
 $CN^- + H_2O \Longrightarrow HCN + OH^-$   
 $NO_2^- + H_2O \Longrightarrow HNO_2^- + OH^-$ 

It is evident from above examples that  $H_2O$  can act both as an acid and a base.  $H_2O$  is thus regarded as amphiprotic.

 $NH_3$  and  $CH_3COOH$  also act as  $\boldsymbol{amphiprotic.}$ 

When an acid loses a proton, the residual part of it has a tendency to regain a proton. Therefore, it behaves as a base.

Acid 
$$\rightleftharpoons$$
 H<sup>+</sup> + Base

The acid and base which differ by a proton are known to form a **conjugate pair**. Consider the following reaction:

$$CH_3COOH + H_2O \Longrightarrow H_3O^+ + CH_3COO^-$$

It involves two conjugate pairs. The acid-base pairs are :

$$\begin{array}{cccc} CH_{3}COOH & \stackrel{-H^{+}}{\Longrightarrow} & CH_{3}COO^{-} & ; & H_{2}O & \stackrel{+H^{+}}{\Longrightarrow} & H_{3}O^{+} \\ & Acid & \stackrel{+H^{+}}{\Longrightarrow} & Base & Base & -H^{+} & Acid \end{array}$$

If in the above reaction, the acid,  $CH_3COOH$  is labelled acid<sub>I</sub> and its conjugate base,  $CH_3COO^-$  as base<sub>I</sub> and the  $H_2O$  is labelled as base<sub>II</sub> and its conjugate acid,  $H_3O^+$  as acid<sub>II</sub>, the reaction can be written as :

$$Acid_I + Base_{II} \Longrightarrow Base_I + Acid_{II}$$

Thus, any acid-base reaction involves two conjugate pairs, *i.e.*, when acid reacts with a base, another acid and base is formed. Some more examples are given below:

$$\begin{array}{c} \text{Acid}_{\text{I}} + \text{Base}_{\text{II}} & \Longrightarrow \text{Acid}_{\text{II}} + \text{Base}_{\text{I}} \\ \text{H}_2\text{O} + \text{NH}_3 & \Longrightarrow \text{NH}_4^+ + \text{OH}^- \\ \text{HCN} + \text{H}_2\text{O} & \Longrightarrow \text{H}_3\text{O}^+ + \text{CN}^- \\ \text{NH}_3 + \text{NH}_3 & \Longrightarrow \text{NH}_4^+ + \text{NH}_2^- \\ \text{H}_2\text{O} + \text{H}_2\text{O} & \Longrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \\ \text{HCl} + \text{NH}_3 & \Longrightarrow \text{NH}_4^+ + \text{Cl}^- \\ \text{HF} + \text{CH}_3\text{COOH} & \Longrightarrow \text{CH}_3\text{COOH}_2^+ + \text{F}^- \\ \text{HCO}_3^- + \text{H}_2\text{O} & \Longrightarrow \text{H}_3\text{O}^+ + \text{CO}_3^2 \\ \text{HNO}_3 + \text{N}_2\text{H}_4 & \Longrightarrow \text{N}_2\text{H}_5^+ + \text{NO}_3 \\ \text{HF} + \text{HNO}_3 & \Longrightarrow \text{H}_2\text{NO}_3^+ + \text{F}^- \\ \text{[Fe(H}_2\text{O)}_6]^{3^+} + \text{H}_2\text{O} & \Longrightarrow \text{H}_3\text{O}^+ + \text{[Fe(H}_2\text{O)}_5\text{(OH)}]^{2^+} \end{array}$$

Thus, every acid has its conjugate base and every base has its conjugate acid. Some commonly occurring conjugate acid-base pairs are listed below:

Acid	Conjugate base	Acid	Conjugate base
$HNO_3$	$NO_3^-$	$H_2SO_4$	$HSO_4^-$
HCl	Cl-	$HSO_4^-$	$SO_4^{2-}$
HBr	Br <sup></sup>	$H_2CO_3$	HCO <sub>3</sub>
H <sub>2</sub> O	OH-	HCO <sub>3</sub>	$CO_3^{2-}$
NH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> S	HS-
CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>	HS <sup>-</sup>	S <sup>2-</sup>
HCN	CN <sup>-</sup>	$H_3PO_4$	$H_2PO_4^-$
NH <sub>3</sub>	$NH_2^-$	$H_2PO_4^-$	$HPO_4^{2-}$
$H_3PO_2$	$H_2PO_2^-$	$HPO_4^{2-}$	$PO_4^{3-}$

It is clear from the given table that Bronsted-Lowry acids and bases can be molecular, cationic or anionic as listed in the following table:

Type	Acid	Base
Molecular	HClO <sub>4</sub> , HNO <sub>3</sub> , H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> ,	NH <sub>3</sub> , N <sub>2</sub> H <sub>4</sub> , PH <sub>3</sub> ,
	CH₃COOH, HCl, H₂O	amines, alcohols.
Cationic	NH <sub>4</sub> <sup>+</sup> , N <sub>2</sub> H <sub>5</sub> <sup>+</sup> , PH <sub>4</sub> <sup>+</sup> ,	$[Fe(H_2O)_5OH]^{2+}$ ,
	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> , Na <sup>+</sup> , Ba <sup>2+</sup>	$[Al(H_2O)_5OH]^{2+}$
Anionic	HCO3, HSO4, HSO3,	CI, Br, CN, NH <sub>2</sub> ,
	HS <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub>	$CO_3^{2-}$ , $SO_4^{2-}$ , $OH^{-}$

There is an advantage of Bronsted-Lowry concept that besides water any other solvent, which has the tendency to accept or lose a proton may decide the acidic or basic behaviour of the dissolved substance in that solvent. Moreover, it can be said that the term acid or base is comparative. A substance may act as an acid in one solvent while it behaves as a base in other solvent. Acetic acid acts as an acid in water but behaves as a base in HF.

On the basis of proton interaction, solvents can be classified into four types :

- (i) Protophilic solvents: Solvents which have the tendency to accept protons, *e.g.*, water, alcohol, liquid ammonia, etc.
- (ii) Protogenic solvents: Solvents which have the tendency to donate protons, e.g., water, liquid hydrogen chloride, glacial acetic acid, liquid hydrofluoric acid, etc.
- (iii) Amphiprotic: Solvents which have both the tendencies to accept or donate protons, e.g., water, liquid ammonia, alcohol, etc.
- (iv) Aprotic: Solvents which neither donate nor accept protons, *e.g.*, benzene, carbon tetrachloride, carbon disulphide, etc.

#### Strength of Acids and Bases

The strength of an acid depends upon its tendency to lose its proton and the strength of the base depends upon its tendency to gain the proton.  $K_a$ , the equilibrium constant, of the following reaction gives a quantitative measure of the strength of the acid.

$$HA + H_2O \Longrightarrow H_3O^+ + A^ K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Larger the value of  $K_a$  indicates that the acid is stronger in nature.

Similarly,  $K_b$  of the following reaction gives the quantitative measure of the strength of the base.

$$B + H_2O \Longrightarrow BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Larger the value of  $K_b$  indicates that the base is stronger in nature.

It is further observed that strong acids have weak conjugate bases while weak acids have strong conjugate bases.

Acid-Base Chart Containing Some Common Conjugate Acid-Base Pairs

•	Acid	Conjugate base		Ka	pK <sub>a</sub>
1	н	Γ .		10 <sup>11</sup>	-11
	HClO <sub>4</sub>	ClO <sub>4</sub>		.10 <sup>10</sup>	-10
	HBr	Br <sup>-</sup>	· C-	10 <sup>9</sup>	-9
	HCI	Cl <sup>-</sup> -		10 <sup>7</sup>	<b>-7</b>
- /	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub>		10 <sup>2</sup>	-2
	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	-5	1	0.0
Increasing order of acid strength	$H_2SO_3$	HSO <sub>3</sub>	î. Increasing order of basic strength	$1.5 \times 10^{-2}$	1.81
stre	HSO <sub>4</sub>	SO <sub>4</sub> <sup>2-</sup>	cstr	$1.2 \times 10^{-2}$	1.92
acid	$H_3PO_4$	H <sub>2</sub> PO <sub>4</sub>	asi	$7.5 \times 10^{-3}$	2.12
rof	HF	F-	, lfar	$3.5 \times 10^{-4}$	3.45
orde	CH₃COOH	CH₃COO⁻	rde	1.8 × 10 <sup>-5</sup>	4.7
mg (	H <sub>2</sub> S	HS <sup>-</sup>	60	1.0 × 10 <sup>-7</sup>	7.0
easi	NH <sup>‡</sup>	NH <sub>3</sub>	easi	$5.6 \times 10^{-10}$	9. <b>3</b>
Inc	HCN	CNT.	Incr	$4.0 \times 10^{-10}$	9. <b>4</b>
	H <sub>2</sub> O	OH-	Table to the same state of the	$1.0 \times 10^{-14}$	14.0
	CH₃OH	CH <sub>3</sub> O⁻		Very small	Large
	NH <sub>3</sub>	NH <sub>2</sub>		Very small	Large

**Note:** In order to avoid writing negative powers of 10,  $K_a$  or  $K_b$  are generally converted into  $pK_a$  ( $-\log_{10} K_a$ ) or  $pK_b$  ( $-\log_{10} K_b$ ) respectively. Smaller the value of  $pK_a$  indicates the stronger acids.

The strength of an acid also depends upon the solvent. The acids  $HClO_4$ , HCl,  $H_2SO_4$  and  $HNO_3$  which have nearly same strength in water, will be in the order of,

$$HClO_4 > H_2SO_4 > HCl > HNO_3$$

in acetic acid, since the proton accepting tendency of acetic acid is much weaker than water. HCl acts as a stronger acid in NH<sub>3</sub>, weak acid in CH<sub>3</sub>COOH, neutral in benzene and a weak base in HF.

#### Levelling and Differentiating Effect

Water is a strong base as it has a great tendency to accept protons from strong acids. Thus, all strong acids such as HClO<sub>4</sub>, HBr, HI, H<sub>2</sub>SO<sub>4</sub>, etc., almost completely react with water and they appear to be equally strong in water. **This effect of water and other strong bases to level all the strong acids to the same strength is known as levelling effect.** Consequently, no acid significantly stronger than H<sub>3</sub>O<sup>+</sup> can survive in water. So, relative strengths of strong acids cannot be determined in water.

An analogous limit can be found for bases in water. Any base *B* that is strong enough to undergo complete protonation by donation from water, leaving OH<sup>-</sup> ions in solution in place of every *B* molecule added, will be levelled. The OH<sup>-</sup> ion is the strongest base that can exist in water because anything stronger immediately forms OH<sup>-</sup> ions by reaction with water. Thus, alkali metal amides and methanides cannot be studied in water because both anions generate OH<sup>-</sup> ions quantitatively and are fully protonated to NH<sub>3</sub> and CH<sub>4</sub>.

$$KNH_2 + H_2O \Longrightarrow K^+(aq) + OH^-(aq) + NH_3(aq)$$
  
 $LiCH_3 + H_2O \Longrightarrow Li^+(aq) + OH^-(aq) + CH_4(q)$ 

When strong acids are dissolved in a weak acid or a weak base, all are not equally ionised and their relative strengths can be differentiated. It is called **differentiating effect**. For example, acetic acid instead of water as a solvent can be used for the grading of strong acids. This is because of the poor proton accepting character of acetic acid. The acidic character of a number of acids when dissolved in glacial acetic acid (solvent) has been determined by measuring degree of dissociation. The acidic character has been found to be in the following order:

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$
.

#### Limitations

- (i) A substance is termed as an acid or base if it reacts with some other substance, *i.e.*, if it donates proton to other substance, it is an acid and if it accepts proton from other substance, it is a base.
- (ii) There are number of acid-base reactions in which no proton transfer takes place, e.g.,

$$SO_2 + SO_2 \Longrightarrow SO^{2+} + SO_3^{2-}$$
  
 $Acid_I \quad Base_{II} \quad Acid_{II} \quad Base_{II}$ 

Thus, the protonic definition cannot be used to explain the reactions occurring in non-protonic solvents such as  $COCl_2$ ,  $SO_2$ ,  $N_2O_4$ , etc.

**Example 1.** *Identify the Bronsted acid and its conjugate base in the following :* 

(a) 
$$PO_A^{3-} + H_2O \Longrightarrow HPO_A^{2-} + OH^{-}$$

(b) 
$$H_2Fe(CO)_4 + CH_3OH \rightleftharpoons [HFe(CO)_4]^- + CH_3OH_2^+$$

(c) 
$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$

$$(d) NH_3 + H_2S \Longrightarrow NH_4^+ + HS^-$$

#### Solution:

In (a),  $H_2O$  transfers a proton to  $PO_4^{3-}$ , thus,  $H_2O$  is Bronsted acid and  $OH^-$  is its conjugate base. In (b),  $H_2Fe(CO)_4$  is an acid as it donates a proton to  $CH_3OH$ . Its conjugate base is  $[HFe(CO)_4]^-$ . In (c),  $HNO_3$  is an acid as it donates a proton to  $H_2O$ .  $NO_3^-$  is its conjugate base.

In (d),  $H_2S$  is an acid as it transfers a proton to  $NH_3$ . Its conjugate base is  $HS^-$ .

**Example 2.** A bottle is marked with 'Acid' pH = 5. Whether the acid is strong or weak? Explain.

#### Solution:

It cannot be predicted on the basis of pH alone whether the acid is strong or weak. pH depends on concentration.

**Example 3.** (a) Liquid  $NH_3$  like water is an amphiproti solvent. Write the equation for the autoionisation of  $NH_3$ .

(b) Aniline is a weak organic base in aqueous solution. Suggest a solvent in which aniline would become a stronger base.

#### Solution:

- (a)  $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$
- (b) Any solvent which has appreciably stronger acidic properties than water would render aniline as a stronger base. Acetic acid is one such solvent.

### 3.4 LEWIS CONCEPT

A more general and fundamental concept of acid-base behaviour was proposed by G.N. Lewis in 1923 (the same year in which Bronsted concept was introduced). However, the concept became influential only in 1930 onwards. According to this concept, a base is a substance which can furnish a pair of electrons to form a coordinate bond whereas an acid is a substance which can accept a pair of electrons. A Lewis acid is a substance that acts as an electron acceptor or electrophile while a Lewis base is a substance that acts as an electron donor or nucleophile. Neutralisation reaction involves the formation of a coordinate bond.

A simple example of an acid-base is the reaction between a proton and a hydroxyl ion.

$$H^+ + : O: H^- \longrightarrow H: O: H$$
Acid Base

Some other examples are:

$$H_3N$$
: +  $BF_3 = H_3N \rightarrow BF_3$ 
 $Base$ 
Acid

 $H^+$  + :N $H_3 = [H \leftarrow NH_3]^+$ 
Acid

 $BF_3$  + :F: = [:F \to BF\_3]

According to Lewis concept, the given species can act as Lewis acids:

(i) Molecules in which the central atom has incomplete octet: Lewis acids are electron deficient molecules such as BF<sub>3</sub>, AlCl<sub>3</sub>, GaCl<sub>3</sub>, etc.

$$H_3N: + AlCl_3 \longrightarrow H_3N \longrightarrow AlCl_3$$

(ii) Molecules in which the central arom has empty *d*-orbitals: The central atom of the halides such as  $SiX_4$ ,  $GeX_4$ ,  $TiCl_4$ ,  $SnCl_4$ ,  $PX_3$ ,  $PF_5$ ,  $SF_4$ ,  $SeF_4$ ,  $TeCl_4$ , etc., have vacant *d*-orbitals. These can, therefore, accept an electron pair and act as Lewis acids.

$$SiF_4 + 2:F:^- \longrightarrow [SiF_6]^{2-}$$
  
Lewis acid Lewis base Complex

(iii) Simple cations: All cations are expected to act as Lewis acids since they are electron deficient in nature. However, cations such as  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , etc., (inert gas configuration) have a very little tendency to accept electrons, while the cations like  $H^+$ ,  $Ag^+$ ,  $Fe^{3+}$ ,  $Cu^{2+}$ , etc., have greater tendency to accept electrons and, therefore, act as Lewis acids.

$$Ag^+ + 2:NH_3 \longrightarrow [H_3N \rightarrow Ag \leftarrow NH_3]^+$$
  
 $Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$ 

(iv) Molecules having a multiple bond between atoms of dissimilar electronegativity: Typical examples of molecules belonging to this class of Lewis acids are  $CO_2$ ,  $SO_2$  and  $SO_3$ . Under the influence of attacking Lewis base, one  $\pi$ -electron pair will be shifted towards the more negative atom.

$$OH$$

$$C = O + OH^{-} \longrightarrow -O - C = O \text{ or } HCO_{3}^{-}$$

**(v) Elements with an electron sextet:** Oxygen and sulphur atoms contain six electrons in their valency shell and can accept a lone pair of electrons and act as Lewis acids.

The following species can act as Lewis bases:

(i) Neutral species having at least one lone pair of electrons: For example, ammonia, amines, alcohols, etc., act as Lewis bases as they contain a pair of electrons.

:NH<sub>3</sub>, 
$$R$$
— $\dot{N}$ H<sub>2</sub>,  $R$ — $\dot{O}$ —H, H— $\dot{O}$ —H,  $R$ — $\dot{O}$ — $R$ 

(ii) Negatively charged species or simple anions: For example, chloride, cyanide, hydroxide ions, etc., act as Lewis bases.

(iii) Multiple bonded compounds: The compounds which form coordination compounds with transition metals such as CO, NO, ethylene, acetylene, etc., can act as Lewis bases.

$$CH_2 = CH_2 + Ag^+ \longrightarrow \begin{bmatrix} CH_2 - CH_2 \\ Ag \end{bmatrix}^+$$

It may be noted that all Bronsted bases are also Lewis bases but all Lewis acids are not Bronsted acids.

#### Limitations of Lewis Concept

- (i) Lewis theory fails to explain the relative strength of acids and bases as different types of reactions are involved.
- (ii) Acids such as HCl, H<sub>2</sub>SO<sub>4</sub> do not form coordinate bonds with bases.
- (iii) All acid-base reactions are fast. However, the formation of coordinate bond is very slow in certain cases.

**Example 4.** (a) What is the Lewis acid and base in the following reaction?

$$2NH_3(aq) + Ag^{\dagger}(aq) \longrightarrow [Ag(NH_3)_2]^{\dagger}(aq)$$

- (b) What allows ethoxyethane to behave as a Lewis base?
- (c) Whether aluminium trichloride is a Lewis acid or a base or both?

#### Solution:

- (a) The silver ion accepts the lone pairs from ammonia. Therefore, Ag<sup>+</sup> is a Lewis acid and ammonia a Lewis base.
- (b) The ether has two lone pairs on the oxygen like water.
- (c) AlCl<sub>3</sub> acts both as a Lewis acid and base, *i.e.*, aluminium atom is the Lewis acid and chlorine the Lewis base. Due to this reason it forms dimer, Al<sub>2</sub>Cl<sub>6</sub>.

**Example 5.** (a) How do you account for the formation of  $S_2O_3^{2-}$  from  $SO_3^{2-}$  and S in terms of Lewis acid theory?

(b) Whether the following reaction is Lewis acid-base reaction or not?

$$Ca + S \longrightarrow Ca^{2+} + S^{2-}$$

#### Solution:

(a) A sulphur atom is electron deficient and can thus be regarded as an acid.  $SO_3^{2-}$  acts as a base.

(b) The reaction is not a Lewis acid-base reaction as it does not form a coordinate bond.

### 3.5. THE LUX-FLOOD CONCEPT

The concept proposed by Lux (1939) and extended by Flood (1947) to explain acid-base reactions in terms of the oxide ion. According to this concept, a base is any substance which gives up oxide ions and an acid is any substance which gains oxide ions.

$$SO_4^{2-} \Longrightarrow SO_3 + O^{2-}$$

$$Base \qquad Acid$$

$$CaO \Longrightarrow Ca^{2+} + O^{2-}$$

$$Base \qquad Acid$$

$$SiO_2 + O^{2-} \Longrightarrow SiO_3^{2-}$$

$$Acid \qquad Base$$

Thus, acids are the oxide ion acceptors, while bases are the oxide ion donors.

The following reactions, thus, involve CaO, PbO as bases and  $SiO_2$ ,  $SO_3$  as acidic oxides which react together to form salts respectively.

$$\begin{array}{cccc} \text{CaO} & + & \text{SiO}_2 & \longrightarrow & \text{CaSiO}_3 \\ \text{Base} & & \text{Acid} & & & \text{Salt} \\ \text{PbO} & + & \text{SO}_3 & \longrightarrow & \text{PbSO}_4 \\ \text{Base} & & \text{Acid} & & & \text{Salt} \\ \end{array}$$

Substances are termed amphoteric if they show a tendency of losing as well as accepting an oxide ion.

$$ZnO + O^{2-} \Longrightarrow ZnO_2^{2-}$$
;  $ZnO \Longrightarrow Zn^{2+} + O^{2-}$   
 $Al_2O_3 + O^{2-} \Longrightarrow 2AlO_2^{-}$ ;  $Al_2O_3 \Longrightarrow 2Al^{3+} + 3O^{2-}$ 

The Lux-Flood concept can be extended to include transfer of any anion, for example, halide, sulphide, etc.

$$3NaF + AlF_3 \xrightarrow{\text{High temp.}} 3Na^+ + AlF_6^{3-}$$

### 3.6 USANOVICH CONCEPT

This concept is an extension of Lewis concept. According to this concept, an acid is any chemical species which reacts with bases, gives up cations or accepts anions or electrons and a base is any chemical species which reacts with acids, gives up anions or accepts cations or donates electrons. Besides, Arrhenius, Bronsted-Lowry or Lewis acids and bases, this concept includes all the oxidising agents as acids

and reducing agent as bases. Some examples of acid-base reactions in terms of this concept are given below:

Acid	Base	Salt	Justification
Cl <sub>2</sub> +	2K →	2KCl	K loses an electron while Cl gains an electron.
SO <sub>3</sub> +	CaO	CaSO <sub>4</sub>	CaO yields $O^{2-}$ and $SO_3$ accepts $O^{2-}$ .
As <sub>2</sub> S <sub>5</sub> +	-3(NH <sub>4</sub> ) <sub>2</sub> S -	$\longrightarrow$ 2(NH <sub>4</sub> ) <sub>3</sub> AsS	4 $(NH_4)_2S$ loses $S^2$ ions while $As_2S_5$ gains $S^2$ ions.
Fe(CN)	2+4KCN -	$\longrightarrow K_4 \text{Fe}(CN)_6$	Fe(CN) <sub>2</sub> combines with CN <sup>-</sup> ions given by KCN.

It is the most general concept out of the concepts of acid-base so far given. The concept is undoubtedly too broad that nearly all the chemical reactions fall into acid-base category.

### 3.7 HARD AND SOFT ACIDS AND BASES

All the Lewis acids and bases are classified as hard and soft acids and bases. It was proposed by **Pearson** in 1963 in order to explain the stability of the complexes formed by the combination of a Lewis acid and a Lewis base.

**Soft bases** have donor atoms which are easily polarised and have low electronegativity. The **hard bases** have properties opposite to those of the soft bases, *i.e.*, hard bases have donor atom with low polarizabilities and high electronegativity. Within a group in the periodic table softness increases with increasing size of the donor atom.

**Hard bases:**  $H_2O$ ,  $OH^-$ ,  $F^-$ ,  $CH_3COO^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $CI^-$ ,  $CO_3^{2-}$ ,  $CIO_4^-$ ,  $NO_3^-$ , ROH,  $RO^-$ ,  $R_2O$ ,  $NH_3$ ,  $RN_2$ ,  $N_2H_4$ .

**Soft bases:**  $R_2$ S, RSH, RS $^-$ ,  $I^-$ , SCN $^-$ ,  $S_2$ O $_3^{2-}$ ,  $R_3$ P,  $R_3$ As,  $(RO)_3$ P, CN $^-$ , RNC, CO,  $C_2$ H $_4$ ,  $C_6$ H $_6$ ,  $H^-$ ,  $R^-$ .

**Border line:**  $C_6H_5NH_2$ ,  $C_5H_5N$ ,  $Br^-$ ,  $NO_2^-$ ,  $SO_3^{2-}$ ,  $N_3^-$ .

**Soft acids** are those which possess acceptor atoms, large in size, of low positive charge, have high polarizability and low electronegativity and do not have noble gas configuration. **Hard acids** are those in which acceptor atoms have small size, high electronegativity, low polarizability and possess noble gas configuration.

**Hard acids:** H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Be<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Mn<sup>2+</sup>, Al<sup>3+</sup>, Ga<sup>3+</sup>, In<sup>3+</sup>, La<sup>3+</sup>, CO<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Ti<sup>4+</sup>, etc.

**Soft acids:** Cu<sup>+</sup>, Ag<sup>+</sup>, Au<sup>+</sup>, Te<sup>+</sup>, Hg<sup>+</sup>, Pd<sup>2+</sup>, Cd<sup>2+</sup>, Pt<sup>2+</sup>, Hg<sup>2+</sup>, GaCl<sub>3</sub>, I<sup>+</sup>, Br<sup>+</sup>, I<sub>2</sub>, Br<sub>2</sub>, etc.

**Border line**: Fe<sup>2+</sup>, CO<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Sn<sup>2+</sup>, Sb<sup>3+</sup>, SO<sub>2</sub>, etc.

The bonding between hard acids and hard bases are predominantly ionic whereas the soft-soft interactions give largely covalent compounds. Hard acids have vacant orbitals and can accept  $\sigma$ -electrons while hard bases with filled outer

valence shell orbitals, can donate the  $\sigma$ -pair of electrons. For weak acids and weak bases,  $\pi$ -bonding seems to be important. The compounds between hard acids and hard bases and between soft acids and soft bases are stable.

# 3.89 SOME GENERAL TRENDS IN ACIDIC AND BASIC PROPERTIES (On the basis of

Arrhenius and Bronsted-Lowry concepts)

In order to analyse the relationship between molecular structure, the acids are divided into two types:

- (i) Covalent hydrides: In these the proton is directly attached with the central atom of the molecule. Examples are: HX(X = F, Cl, Br, I),  $H_2O$ ,  $CH_4$ ,  $H_2S$ , etc. These are also called hydracids or hydroacids.
- (ii) Oxy-acids: In these the proton is attached to an oxygen atom, the later being bonded to the central atom. Examples are: H<sub>2</sub>SO<sub>3</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, etc.

### (i) Covalent hydrides:

Two factors influence the acid strength of the hydride of an element: The electronegativity of the element and the atomic size of the element. The first of these factors is best understood by comparing the hydrides of the elements of a period of the periodic table. The second is important when group comparisons of the periodic table are made.

(a) Hydrides of the elements of a period: The acid strengths of the hydrides of the elements of a period increase from left to right in the same order as electronegativity increases. Highly electronegative element withdraws electrons from the hydrogen easily and facilitate the release of hydrogen as proton. The electronegativities of the following second and third period elements fall in the order:

$$N < O < F$$
 and  $P < S < C1$ 

The acid strength of the hydrides increases in the same order:

$$NH_3 < H_2O < HF$$
 and  $PH_3 < H_2S < HC1$ 

The increase in acidic nature is also due to the fact that the stability of their conjugate bases increases in the order:

$$NH_2^- < OH^- < F^-$$

The increase in acidic properties is supported by successive increase in the dissociation constant.

$$NH_3(=10^{-35}) < H_2O(=10^{-14}) < HF(=10^{-4})$$

**(b) Hydrides of the elements of a group:** The acidity of the hydrides of the elements of a group increases with increasing size of the central atom. For example in the hydrides of VIA or XVI group and VIIA or XVII group, the acidic nature increases as the atomic number of the central element increases.

$$H_2O < H_2S < H_2Se < H_2Te$$

and HF < HCl < HBr < HI

The two factors which influence acid strength work against each other in these hydrides. The effect of atomic size outweighs the electronegativity effect. A proton is more easily removed from a hydride in which the central atom is larger than from one in which the central atom is small. The charge density on the conjugate base is in the order:

$$O^{2-} > S^{2-} > Se^{2-} > Te^{2-}$$
  
and  $F^- > Cl^- > Br^- > l^-$ 

Greater charge density on the conjugate base will result in greater proton attraction.

The acidic nature of the hydrides of VIIA group elements is also explained by the fact that bond energies decrease.

$$H - F > H - Cl > H - Br > H - I$$
135 kcal mol<sup>-1</sup> 103 kcal mol<sup>-1</sup> 88 kcal mol<sup>-1</sup> 71 kcal mol<sup>-1</sup>

Due to large electronegativity, hydrogen bonding exists in the hydrides of oxygen and fluorine which also decreases their acid strength.

In the hydrides of the elements having nearly the same electronegativity, the acidic nature increases as the size of the central element increases. C, S and I possess same electronegativity, the acidic nature follows the following order:

$$CH_4 < H_2S < HI$$

as the size increases from carbon to iodine.

#### 🕍 (ii) Oxy-acids:

In oxy-acids, the proton is attached to oxygen atom which is linked to the central atom.

$$H \stackrel{a}{\longrightarrow} O \stackrel{b}{\longrightarrow} Z$$

The main factors which affect the strength of an oxy-acid are: (a) the size of the central atom, (b) the electronegativity of the central atom and (c) the number of other electronegative atoms attached to the central atom.

Smaller the size and greater the electronegativity of Z make the oxy-acid stronger. These factors will shift the electron pair between Z and O towards Z and this displacement will in turn cause a shifting of electron pair between oxygen and hydrogen towards oxygen. Thus, O—H bond is weakened and proton is easily released. In the series,

The electronegativity increases and size decreases of the central element. Same trend is observed in the oxy-acids of different elements in the same oxidation state  $HClO_4 > HBrO_4 > HIO_4$ .

Greater the number of negative atoms present in the oxyacid make the acid stronger. In general, the strengths of acids that have general formula,

$$(HO)_m ZO_n$$

can be related to the value of n.

If n = 0, the acid is very weak, HOCl, (HO)<sub>3</sub>B, (HO)<sub>4</sub>Si. If n = 1, the acid is weak, HOClO, HONO, (HO)<sub>2</sub>SO, (HO)<sub>3</sub>PO.

If n = 2, the acid is strong, HOClO<sub>2</sub>, HONO<sub>2</sub>, (HO)<sub>2</sub>SO<sub>2</sub>. If n = 3, the acid is very strong, HOClO<sub>3</sub>, HOIO<sub>3</sub>.

The negative atoms draw electrons away from the Z-atom and make it more positive. The Z-atom, therefore, becomes more effective in withdrawing electron density away from the oxygen atom that is bonded to hydrogen. In turn, the electrons of H—O bond are drawn more strongly away from the H-atom. The net effect makes it easier for the proton release and increases the acid strength.

This effect is illustrated by the following series of acids:

**Note:** In the above examples, it is evident that strength of the acid increases as the oxidation number of the central atom increases. However, this rule fails in oxy-acids of phosphorus,

$$H_3^{+1}PO_2$$
 ;  $H_3^{+3}PO_3$  ;  $H_3^{+5}PO_4$ 

as all are weak acids, *i.e.*, about the equal strength. Thus, prediction on the basis of oxidation number is **incorrect**. Formal charge on the central atom gives more reliable prediction. The strength of the acid increases as the formal charge on the central atom increases.

Formal charge = Group number – number of bonds – number of unshared electrons.

As the formal charge is same, all the above oxy-acids of phosphorus are nearly of equal strength.

#### Strength of Bases

(a) Among alkali and alkaline earth metals oxides and hydroxides, the basic nature increases as the size of the central atom increases, *i.e.*, electropositive nature increases.

$$CsOH > RbOH > KOH > NaOH > LiOH$$
  
 $Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$ 

(b) Among the hydrides of the same group, the basic nature decreases with increase in the size of central atom as the tendency to accept proton decreases due to decrease in electron density (or ability to donate the electron pair decreases).

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$
Basic Less basic Neutral

(c) The larger the size of the atom holding the unshared electrons, the lesser is the availability of the electrons, *i.e.*, the basic strength of halide ions follow the following order:

(d) The basic nature of a substance decreases with the increase of the electronegativity of the atom holding the lone pair of electrons, *i.e.*, the tendency to donate the electron pair to proton decreases with increase of electronegativity.

$$:NH_3 > H_2O: > HF:$$

(e) The presence of a positive charge on the atom holding the lone pair decreases the base strength while a negative charge increases the base strength.

$$:OH>H-O-H>H_3O^{\dagger}:$$

(f) Base strength increases with decrease in oxidation state of the central atom.

$$NH_3 > N_2H_4$$
 ;  $PH_3 > P_2H_4$  Oxid. Number -3 -2 -3 -2

#### **Amphoterism**

Similarly,

Substances which behave as bases towards strong acids and acids towards strong bases are called **amphoteric** and the phenomenon as **amphoterism**. Some metal oxides and hydroxides are amphoteric. For example, ZnO and Zn(OH)<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Al(OH)<sub>3</sub>, SnO and Sn(OH)<sub>2</sub>, PbO and Pb(OH)<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub> and Cr(OH)<sub>3</sub> are amphoteric in nature.

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$
  
 $ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$   
 $Sn(OH)_2 + 2HCl \longrightarrow SnCl_2 + 2H_2O$   
 $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$ 

The salts of Zn<sup>2+</sup>, Sn<sup>2+</sup>, Pb<sup>2+</sup>, Al<sup>3+</sup> and Cr<sup>3+</sup> dissolve in excess of NaOH solution due to formation of hydroxide first.

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$$
  
 $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$ 

**Example 6.** Explain on the basis of SHAB principle,

- (a)  $Ag(CN)_2^-$  is stable while  $AgCl_2^-$  is unstable.
- (b) The alkaline earth metals are found in nature as carbonates and sulphates whereas mercury and silver are found as sulphides.

#### Solution:

(a)  $Ag^+$  is a soft acid,  $CN^-$  is a soft base while  $Cl^-$  is a hard base. Therefore,  $Ag(CN)_2^-$  (soft acid + soft base) is a stable complex while  $AgCl_2^-$  (soft acid + hard base) is an unstable complex.

(b) The ions  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Ba^{2+}$ , etc., are hard acids while  $SO_4^{2-}$  and  $CO_3^{2-}$  ions are also hard bases. Since compounds of hard acids and hard bases are stable, alkaline earth metals are found in nature as sulphates and carbonates. However,  $Hg^{2+}$  and  $Ag^+$  ions are soft acids. They combine with soft bases such as  $S^{2-}$  to form stable compounds.

#### **Example 7.** Explain the following:

- (a) Br ion is a Lewis as well as Bronsted base.
- (b) NH<sub>3</sub> is a Lewis as well as Bronsted base.
- (c) BF<sub>3</sub> is a Lewis acid but not a Bronsted acid.

#### Solution:

- (a) Br ion contains lone pair of electrons which it can donate. Hence, it acts as a Lewis base. Br can accept proton and hence, it acts as a Bronsted base.
  - (b) NH<sub>3</sub> acts as a Lewis base as the nitrogen possesses a lone pair of electrons which it can donate (H<sub>3</sub>N → BF<sub>3</sub>). It can combine with H<sup>+</sup> to form ammonium, NH<sub>4</sub><sup>+</sup> ion. Hence, it is a Bronsted base.
  - (c) BF<sub>3</sub> acts as a Lewis acid as it is an electron pair acceptor (H<sub>3</sub>N: + BF<sub>3</sub> → H<sub>3</sub>N → BF<sub>3</sub>). BF<sub>3</sub> does not possess the tendency to lose a proton, hence it is not a Bronsted acid.

# SUMMARY AND IMPORTANT POINTS TO REMEMBER



- 1. The word acid is a Latin word-acidus meaning sour.
- Liebig, in 1830, defined acid as a compound which contains one or more hydrogen atoms replaceable partially or completely by a metal or a positive radical to produce a salt
- 3. According to Arrhenius concept, all substances which give H<sup>+</sup> ions when dissolved in water are called acids while those which ionise in water to furnish OH<sup>-</sup> ions are called bases. The reaction between an acid and a base is termed neutralisation, i.e., neutralisation involves the reaction between H<sup>+</sup> and OH<sup>-</sup> ions to form water.

#### Limitations

- It is applicable to aqueous solutions only, i.e., water is necessary to explain the acidic or basic properties of the substances.
- (ii) It fails to explain acidic properties of non-protic compounds such as SO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, etc.
- (iii) It fails to explain the basic nature of compounds like NH<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, etc.
- (iv) It fails to explain the acidic nature of salts like AlCl<sub>3</sub> in aqueous solution.
- 4. Modified Arrhenius concept rectifies most of the limitations. Water is a weak electrolyte and neutral in nature, i.e., [H<sub>3</sub>O<sup>+</sup>] = [OH<sup>-</sup>].

The substances which increase the concentration of  $\mathrm{H_3O^+}$  ions in water act as acids while those which increase the concentration of  $\mathrm{OH^-}$  ions act as bases.  $\mathrm{SO_2}$  is thus an acid and  $\mathrm{NH_3}$  is a base.

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H_3O^+ + HSO_3^-$$
  
 $NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$ 

- The strength of an acid or a base in Arrhenius concept is based on the extent of ionisation, i.e., on the equilibrium constant of an acid, K<sub>a</sub>, and on the equilibrium constant of a base, K<sub>b</sub>.
- 6. According to Bronsted-Lowry concept, a substance is known as an acid if it can donate a proton and as a base if it can accept a proton. Acids are proton donors (protogenic) and bases are proton acceptors (protophilic).

Chemical species that differ in composition only by proton are called a conjugate pair.

Acid 
$$\rightleftharpoons$$
 H<sup>+</sup> + Base

Every acid has its conjugate base. If acid is strong, its conjugate base is strong and *vice-versa*. An acid base reaction involves two conjugate pairs, *i.e.*, when acid reacts with a base another acid and base are formed.

H<sub>2</sub>O can act either as an acid or a base (amphiprotic).

- **8.** HCO<sub>3</sub>, HSO<sub>4</sub>, H<sub>2</sub>PO<sub>4</sub>, HPO<sub>4</sub>, H<sub>2</sub>PO<sub>3</sub> and HSO<sub>3</sub> are amphiprotic in nature.
- **9.** Solvents which neither donate nor accept protons, *e.g.*, benzene, carbon tetrachloride, carbon disulphide, etc., are called aprotic solvents.
- 10. The strength of an acid depends upon its tendency to lose its proton and the strength of the base depends upon its tendency to gain the proton.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- : B + H_2O \rightleftharpoons H^+B + OH^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$
  $K_b = \frac{[H^+B][OH^-]}{[B]}$ 

Larger the value of  $K_a$  indicates that the acid is stronger in nature.

Larger the value of  $K_b$  indicates that the base is stronger in nature.

The strength of an acid also depends on the solvent. The acids  $HClO_4$ , HCl,  $H_2SO_4$  and  $HNO_3$  which have nearly same strength in water, will be in the order of :

$$HClO_4 > H_2SO_4 > HCl > HNO_3$$

in acetic acid. HCl acts as a stronger acid in NH<sub>3</sub>, weak acid in acetic acid, neutral in benzene and weak base in HF. In order to avoid writing negative powers,  $K_a$  or  $K_b$  are generally converted into p $K_a$  ( $-\log_{10} K_a$ ) or p $K_b$  ( $-\log_{10} K_b$ ) respectively. Smaller the value of p $K_a$  indicates the stronger acid.

11. Any species, that is an acid by Arrhenius concept remains an acid in the Bronsted-Lowry concept. The same is true for

bases. Certain species which do not contain  $OH^-$  group which are not regarded as bases by Arrhenius concept such as  $HCO_3$ ,  $H_2PO_4$ , etc., are regarded as bases by Bronsted-Lowry concept.

12. According to Lewis concept, a base is a substance which can furnish a pair of electrons to form a coordinate bond whereas an acid is a substance which can accept a pair of electrons. Lewis acid is an electron acceptor, i.e., electrophile while a Lewis base is an electron donor or nucleophile. Lewis acid is electron deficient while Lewis base is electron rich species (lone pair of electrons).

The following species can act as Lewis acids:

- (i) Molecules in which central atom has incomplete octet such as: BF<sub>3</sub>, AlCl<sub>3</sub>, GaCl<sub>3</sub>, etc.
- (ii) Molecules in which central atom has empty d-orbitals such as : SiX<sub>4</sub>, SnCl<sub>4</sub>, PF<sub>5</sub>, SF<sub>4</sub>, PX<sub>3</sub>, etc.
- (iii) Simple cations such as : H<sup>+</sup>, Ag<sup>+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, etc., have a tendency to accept electrons.
- (iv) Molecules having a multiple bond between atoms of dissimilar electronegativity such as: CO<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>, etc.
- (v) Elements with an electron sextet such as oxygen and sulphur atoms.

The following species can act as Lewis bases:

- (i) Neutral species having at least one lone pair of electrons such as: NH<sub>3</sub>, R—NH<sub>2</sub>, R—O—H, etc.
- (ii) Negatively charged species or simple anions such as :  $Cl^-$ ,  $CN^-$ ,  $OH^-$ , etc.
- (iii) Multiple bonded compounds such as : CO, NO, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, etc.

It may be noted that all Bronsted bases are also Lewis bases but all Lewis acids are not Bronsted acids.

13. According to Lux-Flood concept, a base is any substance which gives up oxide ions and an acid is any substance which gains oxide ions. Thus, acids are the oxide acceptors, while bases are oxide ion donors.

$$SO_4^{2-} \iff SO_3 + O^{2-}$$
 ;  $SiO_2 + O^{2-} \iff SiO_3^{2-}$   
Base Acid Acid Base

- 14. According to Usanovich concept, an acid is any chemical species which reacts with bases, gives up cations or accepts anions or electrons while a base is any chemical species which reacts with acids, gives up anions or accepts cations or donates electrons. This concept is an extension of Lewis concept. This concept regards all oxidising agents as acids and reducing agents as bases.
- 15. All the Lewis acids and bases are classified as hard and soft acids and bases. It was proposed by Pearson in 1963. Soft bases have donor atoms which are easily polarised and have low electronegativity such as: RSH, I<sup>-</sup>, R<sub>3</sub>P, CN<sup>-</sup>, etc.

Hard bases have donor atoms which have high electronegativity and low polarizabilities such as :  $H_2O$ ,  $OH^-$ ,  $F^-$ ,  $CI^-$ ,  $CO_3^{2-}$ ,  $NH_3$ , etc.

**Soft acids** are those which have acceptor atoms, large in size, low electronegativity, low positive charge and do not have noble gas configuration. These possess high polarizability. The examples are:  $Ag^+$ ,  $Au^+$ ,  $Cd^{2+}$ ,  $Sn^{2+}$ ,  $Hg^{2+}$  and  $I^+$ , etc.

Hard acids are those in which atoms have small size, high electronegativity, low polarizability and possess noble gas configuration. The examples are :  $H^+$ ,  $Li^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mn^{2+}$ ,  $Al^{3+}$  and  $Ti^{4+}$ , etc.

The bonding between hard acids and hard bases are predominantly ionic whereas the soft-soft interactions give largely covalent compounds. All these compounds are stable.

#### 16. Trends in acidic and basic properties:

Acids are divided into two types:

- Covalent hydrides: In these, proton is directly attached to the central atom of the molecule.
- (ii) Oxy-acids: In these, proton is attached to an oxygen atom, the later being bonded to the central atom.
- Covalent hydrides: Two factors influence the acid strength, the electronegativity and the size of the central atom.
  - (a) The acid strength of the hydrides of the elements of a period increases from left to right as the electronegativity increases. Highly electronegative element withdraws the electrons from the hydrogen easily and facilitate the release of hydrogen as proton.

$$NH_3 < H_2O < HF$$
 and  $PH_3 < H_2S < HCl$   
Acidic nature increases.

(b) The acid strength of the hydrides of the elements of a group increases with increasing size of the central atom.

$$H_2O < H_2S < H_2Se < H_2Te$$
  
 $HF < HCl < HBr < HI$ 

Acid strength increases as the size increases.

- 2. Oxy-acids: The main factors which affect the acid strength of an oxy-acid are:
  - (a) The size of central atom,
  - (b) The -electronegativity,
  - (c) The number of other electronegative atoms attached to the central atom.

Smaller the size and greater the electronegativity of central atom make the oxy-acid stronger. These factors shift the electron pair of the bond of oxygen towards central atom and this displacement will in turn cause a shifting of electron pair between oxygen and hydrogen towards oxygen. Thus, O—H bond is weakened and proton is easily released.

oxy-acid make the acid stronger. In general, the strengths of the acids that have general formula,

$$(HO)_m ZO_n$$

can be related to the value of n.

If n = 0, the acid is very weak Example HOCl

If n = 1, the acid is weak Example HOClO

If n = 2, the acid is strong Example HOClO<sub>2</sub>

If n = 3, the acid is very strong Example HOClO<sub>3</sub>

[Formal charge on the central atom gives more reliable prediction about the strength of acid. The strength increases as the formal charge on the central atom increases. In the case of oxy-acids of phosphorus, the acid strength of the following oxy-acids is nearly same as formal charge is +1 in them:

$$H_3PO_2$$
  $H_3PO_3$   $H_3PO_4$ ]

#### Strength of Bases

(a) Among alkali and alkaline earth metals the basic nature of oxides and hydroxides increases as the size of the cation increases, *i.e.*, electropositive nature increases.

LiOH < NaOH < KOH < RbOH < CsOH strength increases

 $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$ strength increases

(b) Among the hydrides of the same group, the basic nature decreases.

$$\begin{array}{ccc} NH_3 &> PH_3 &> \underbrace{AsH_3 > SbH_3 > BiH_3}_{Neutral} \end{array}$$

(c) The presence of a positive charge on the atom holding the lone pair decreases the base strength while the negative charge increases the base strength.

# -•••- PRACTICE PROBLEMS -•••-

### Subjective Type Questions

- 1. In the following equations, label each species as an acid or a base. Show the conjugate acid-base pairs.
  - (a)  $HCO_3^-(aq) + HF(aq) \Longrightarrow H_2CO_3(aq) + F^-(aq)$
  - (b)  $HCO_3^-(aq) + OH^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l)$
- 2. In the following reactions, identify the Lewis acid and the Lewis base.
  - (a)  $Ag^+ + 2NH_3 \Longrightarrow Ag(NH_3)_2^+$
  - (b)  $B(OH)_3 + H_2O \implies B(OH)_4^- + H^+$

(c) 
$$BF_3 + CH_3OH \Longrightarrow F_3B:O-CH_3$$

- (d)  $O^{2-} + CO_2 \rightleftharpoons CO_3^{2-}$
- Identify each of the following as an acid or a base in terms of the Arrhenius concept.
  - (a) BaO (b) H<sub>2</sub>S (c) CH<sub>2</sub>NH<sub>2</sub> (d) SO<sub>2</sub>
- 4. Give the conjugate acids of :
  - (i)  $HCO_3^-$  (ii)  $HSO_4^-$
- (iii) [Fe(H<sub>2</sub>O)<sub>5</sub>(OH)]<sup>2+</sup>

- (iv) OH
- (v) SO<sub>3</sub><sup>2-</sup>
- (vi) N<sub>2</sub>H<sub>4</sub>

- (vii) Br
- (viii) CH<sub>3</sub>NH<sub>2</sub>
- (ix) PH<sub>3</sub>

[Hint: In each case the conjugate acid is formed by addition of a proton.]

- 5. Give the conjugate base of:
  - (i) OH
- (ii) NH<sub>3</sub>
- (iii) H<sub>2</sub>O

- (iv) H<sub>3</sub>O<sup>+</sup>
- (v) HCO<sub>3</sub> (viii) HS
- (vi) CH<sub>3</sub>COOH (ix) HNO<sub>3</sub>

(vii) C<sub>2</sub>H<sub>5</sub>OH (viii) HS (ix) HNO<sub>3</sub>
 [Hint: In each case, the conjugate base is formed by loss of a proton.]

6. Label the conjugate acids and bases in these reactions :

(i) 
$$S^{2-} + H_3O^+ \rightleftharpoons HS^- + H_2O$$

(ii) 
$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$$

(iii) 
$$NH_2 + H_2O \rightleftharpoons NH_3 + OH^-$$

(iv) 
$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

(v) 
$$[AI(H_2O)_6]^{3+} + H_2O \rightleftharpoons [AI(H_2O)_5OH]^{2+} + H_3O^+$$

(vi) 
$$CO_3^2 + H_2O \rightleftharpoons HCO_3 + OH^2$$

- (vii)  $PO_4^{3-} + H_2O \Longrightarrow HPO_4^{2-} + OH^{-}$
- (viii)  $H_2Fe(CO)_4 + CH_3OH \implies [HFe(CO)_4]^- + CH_3OH_2^-$
- (ix)  $HSO_4^- + OH^- \iff SO_4^{2-} + H_2O$
- 7. Write down the conjugate acid and base of :
  - (i) NH<sub>3</sub> (ii)
- (ii) HCO<sub>3</sub>
- (iii) HSO<sub>4</sub>
- (iv) H<sub>2</sub>O (v) CH<sub>3</sub>COOH
- (vi) H<sub>2</sub>NCH<sub>2</sub>COOH
- (vii) HS (viii) OH
- 8. In the reactions, which reactant is the Lewis acid and which is the Lewis base?
  - (i)  $NH_3 + BF_3 \longrightarrow H_3N : BF_3$
  - (ii)  $\operatorname{BeF}_{2} + 2F^{-} \longrightarrow \operatorname{BeF}_{4}^{2-}$
  - (iii)  $S + SO_3^{2-} \longrightarrow S_2O_3^{2-}$
  - (iv)  $(CH_3)_3N + SO_3 \longrightarrow (CH_3)_3N : SO_3$
  - (v)  $Fe^{2+} + 6CN^{-} \longrightarrow [Fe(CN)_{6}]^{4-}$
  - (vi)  $CO_2 + OH^- \longrightarrow HCO_3$
- 9. Would each of the following species in solution tend to produce a basic, a neutral or an acidic solution?
  - (a)  $C_2H_3O^-$
- (b) Na<sup>+</sup>
- (c) SO<sub>3</sub><sup>2</sup>
- (d) F

- (e) NH<sub>4</sub>
- (f) AlCl<sub>3</sub>

[Hint: A conjugate of a weak acid produces an alkaline solution whereas a conjugate of a weak base produces an acidic solution. The aqueous solution of a species whose conjugate is strong, is neutral.]

10. Which of the following pairs is the strongest acid? Give reason for your choice:

- (a) [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>
- or  $[Fe(H_2O)_6]^{2+}$
- (b)  $[Al(H_2O)_6]^{3+}$
- or
- [Ga(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> Ge(OH)<sub>4</sub>

HClO<sub>4</sub>

H<sub>2</sub>SO<sub>4</sub>

- (c) Si (OH)<sub>4</sub> (d) HClO<sub>3</sub>
- or
  - or
- (e) H<sub>2</sub>CrO<sub>4</sub>
- or HMnO<sub>4</sub>
- (f) H<sub>3</sub>PO<sub>4</sub>

litmus to red?

- .
- 11. Answer the following :(i) What is the nature of the solution which turns blue

- (ii) What is the nature of the solution which turns red litmus to blue?
- (iii) Conjugate acid-base pair differ by ......
- (iv) Arrhenius theory of acids-bases is not applicable to
- (v) AlCl<sub>3</sub> is a Lewis acid because it is .........
- (vi) NH3 is a Lewis base because it is ..........
- (vii) The ligands in the complex compound are ......
- (viii) A substance gives H<sub>3</sub>O<sup>+</sup> ions in aqueous solution. What is that substance?
- (ix) The conjugate base of a strong acid is ......
- (x) In a reaction H+ ions combine with OH- ions to form water. What is the type of reaction?
- Arrange the following in the order of their:
  - (a) increasing acid strength HF, HCl, HBr and HI
  - (b) increasing acid strength HClO<sub>4</sub>, HClO<sub>3</sub>, HClO<sub>2</sub>, HClO
  - (c) increasing basic nature H<sub>2</sub>O, OH<sup>-</sup>, CH<sub>3</sub>OH, CH<sub>3</sub>O<sup>-</sup> [L.I.T. 1992]
  - (d) increasing acid character CO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, SO<sub>3</sub> [I.I.T. 1988]
  - (e) increasing basic strength ClO, ClO<sub>2</sub>, ClO<sub>3</sub>, ClO<sub>4</sub>
  - (f) increasing acid strength  $[Na(H_2O)_n]^+$ ,  $[Ca(H_2O)_n]^{2+}$ ,  $[Al(H_2O)_6]^{3+}$ ,  $[Fe(H_2O)_6]^{3+}$
  - (g) increasing basic strength F, OH, CH, NH2
  - (h) increasing acid strength CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and HF
  - (i) increasing basic strength H<sub>3</sub>O<sup>+</sup>, H<sub>2</sub>O, OH<sup>-</sup>
  - (j) increasing basic strength CH<sub>3</sub>OH, CH<sub>3</sub>NH<sub>2</sub>, CH<sub>3</sub>F
- Predict the direction of the following reactions in aqueous solution:
  - $HNO_2 + CN^- \Longrightarrow HCN + NO_2$
  - $F^- + H_2O \Longrightarrow HF + OH^-$ (b)
  - $Na^+ + H_2O \Longrightarrow NaOH + H^+$ (c)
- Define and give one example each of the following terms:
  - (a) Bronsted-Lowry acid
- (b) Bronsted-Lowry base
- (c) Lewis acid
- (d) Lewis base
- (e) Amphoteric compound
- (f) Neutralisation
- (g) Hard acid
- (h) Soft base

#### 15. Explain giving reasons:

- (i) CCl4 does not act as a Lewis acid while SiCl4 and SnCl<sub>4</sub> do so.
  - [Hint: Carbon does not have d-orbitals to accommodate the accepted electron pair while Si and Sn possess d-orbitals and thus, accept electron pair electrons.

$$\operatorname{SnCl}_4 + 2 : \text{Ci} : \longrightarrow [\operatorname{SnCl}_6]^{2-}]$$
Lewis acid

(ii) BF<sub>3</sub> acts as a Lewis acid whereas NF<sub>3</sub> does not.

[Hint: BF3 is an electron deficient compound. It can accept an electron pair. N in NF3 has completed octet and d-orbitals are not present. It cannot accept an electron pair.]

(iii) HClO<sub>4</sub> is stronger acid than H<sub>2</sub>SO<sub>4</sub>.

[Hint: The number of terminal oxygen atoms in HClO<sub>4</sub> are three while in H2SO4 are two. Chlorine is more electronegative than S.]

(iv) Water behaves as an acid and also like a base on the basis of protonic concept.

[Hint: With strong acid, water behaves as a base as it accepts proton.

$$HCl + H_2O \iff H_3O^+ + Cl^-$$

With strong base, water behaves as an acid as it donates proton.

$$NH_2^- + H_2O \implies NH_3 + OH^-$$
]

(v) Neither pure H<sub>2</sub>SO<sub>4</sub> nor pure HClO<sub>4</sub> conducts electric current but a mixture of the two does.

[Hint: Both the pure acids are unionised. However, when mixed the stronger acid, HClO<sub>4</sub>, donates a proton to H<sub>2</sub>SO<sub>4</sub> and ions are formed.

$$HClO_4 + H_2SO_4 \rightleftharpoons H_3SO_4 + ClO_4$$

(vi) AgI<sub>2</sub> complex is more stable than AgF<sub>2</sub>.

[Hint: Ag+ ion is a soft acid. Its interaction with I ion, a soft base, yields a stable complex whereas its interaction with F ion, hard base yields an unstable complex.)

(vii) CsF reacts with LiI even though both are ionic.

[Hint: The reaction is an interesting example of preferential combination of soft-soft and hard-hard

(viii) SO<sub>3</sub> has acidic behaviour.

[Hint: Sulphur atom is attached with three very highly electronegative oxygen atoms. As a result, electrons are drawn towards oxygen atoms and S-atom remains with low electron density and thus, has the tendency to accept electrons. So, it acts as a Lewis acid.]

(ix) H<sub>3</sub>PO<sub>4</sub> is tribasic but H<sub>3</sub>PO<sub>3</sub> is dibasic in aqueous solution.

lHint: In H<sub>3</sub>PO<sub>4</sub>, three hydrogen atoms are bonded to phosphorus atom through oxygen atoms and these three hydrogen atoms are dissociated into H+ ion. Hence, H<sub>3</sub>PO<sub>4</sub> is tribasic. In H<sub>3</sub>PO<sub>3</sub>, two hydrogen atoms are bonded to phosphorus atom through oxygen atoms. So, H<sub>3</sub>PO<sub>3</sub> is dibasic.]

(x) Dilute sulphuric acid is said to be stronger than concentrated sulphuric acid.

Hint: Strength of the acid depends on the number of H<sup>+</sup> ions present in the solution. Degree of dissociation, i.e., the tendency to liberate H+ ions increases with dilution. Thus, dil. H2SO4 is stronger than conc. H<sub>2</sub>SO<sub>4</sub>.]

### Matching Type Questions

#### Match the following:

- (a)  $BF_3$
- (i) Cationic Bronsted base
- (b) NH<sub>4</sub>
- (ii) Cl
- (c) H<sub>2</sub>O
- (iii) H<sub>3</sub>PO<sub>2</sub>
- (d) [Al(H<sub>2</sub>O)<sub>5</sub>OH]<sup>2+</sup>
- (iv) Ag<sup>+</sup>
- (e) Monobasic acid Soft acid
- (v) Bronsted acid (vi)  $H^+ + OH^- \rightleftharpoons H_2O$
- (g) Hard base
- (vii) Lewis acid
- (h) Neutralisation
- (viii) Amphiprotic

# tuswers

#### **Answers**: Subjective Type Questions

- 1. (a) H<sub>2</sub>CO<sub>3</sub> and HCO<sub>3</sub> are a conjugate acid-base pair. HF and F are a conjugate acid-base pair.
  - (b) HCO<sub>3</sub> and CO<sub>3</sub><sup>2</sup> are a conjugate acid-base pair. H<sub>2</sub>O and OH are a conjugate acid-base pair.
- $Ag^+ + 2: NH_3 \Longrightarrow [Ag(:NH_3)_2]^+$ 2. (a) Ag+ Lewis acid NH<sub>3</sub> Lewis base
  - (b) B(OH)<sub>3</sub> Lewis acid

$$\begin{array}{cccc} \text{OH} & \text{H} & \text{OH} \\ & & & & \\ \text{HO-B} & + & \text{O:H} & \longrightarrow & \text{HO-B:OH} & +\text{H}^+ \\ & & & & & \\ \text{OH} & & & & \text{OH} \end{array}$$

(d) 
$$CO_2$$
 Lewis acid  $\begin{bmatrix} \vdots \vdots \end{bmatrix}^{2-} + \begin{bmatrix} \vdots \\ \vdots \end{bmatrix} \begin{bmatrix} \vdots \\ \vdots \end{bmatrix}^{2-} + \begin{bmatrix} \vdots \\ \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \\ \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \\ \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \\ \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \\ \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \\ \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots \end{bmatrix} \end{bmatrix} \begin{bmatrix} \vdots$ 

O<sup>2</sup>- Lewis base

- 3. (a) BaO is a base; BaO +  $H_2O \longrightarrow Ba^{2+} + 2OH^-$ 
  - (b)  $H_2S$  is an acid;  $H_2S + H_2O \longrightarrow H_3O^+ + HS^-$
  - (c)  $CH_3NH_2$  is a base;  $CH_3NH_2 + H_2O \longrightarrow CH_3NH_3^+ + OH^-$
  - (d)  $SO_2$  is an acid;  $SO_2 + 2H_2O \longrightarrow H_3O^+ + HSO_3^-$
- 4. (i)  $H_2CO_3$ , (ii)  $H_2SO_4$ , (iii)  $[Fe(H_2O)_6]^{3+}$ , (iv)  $H_2O$ , (v)  $HSO_3$ , (vi)  $N_2H_5^+$ , (vii) HBr, (viii)  $CH_3NH_3^+$ , (ix)  $PH_4^+$ .
- 5. (i)  $O^{2-}$ , (ii)  $NH_{2-}^{-}$ , (iii)  $OH_{2-}^{-}$ , (iv)  $H_{2}O$ , (v)  $CO_{3-}^{2-}$ , (vi)  $CH_{3}COO^{-}$ , (vii)  $C_2H_5O^-$ , (viii)  $S^{2-}$ , (ix)  $NO_3^-$ .

	Conjugate Acid	pairs Base	Conjugate Acid	pairs Base
(i)	HS <sup>-</sup>	S <sup>2</sup>	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O
(ii)	$N_2H_5^+$	$N_2H_4$	$H_2O$	$OH^-$
(iii)	NH <sub>3</sub>	$NH_2^-$	H <sub>2</sub> O	OH-
(iv)	CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>	$H_3O^+$	$H_2O$
(v)	$[Al(H_2O)_6]^{3+}$	$[Al(H_2O)_5(OH)]^{2+}$	$H_3O^+$	$H_2O$
(vi)	HCO <sub>3</sub>	CO <sub>3</sub> <sup>2</sup> -	$H_2O$	OH"
(vii)	$HPO_4^{2-}$	PO <sub>4</sub> <sup>3-</sup>	H <sub>2</sub> O	$OH^-$
(viii)	H <sub>2</sub> Fe(CO) <sub>4</sub>	[HFe(CO) <sub>4</sub> ]	$CH_3OH_2^+$	CH <sub>3</sub> OH
(ix)	HSO <sub>4</sub>	SO <sub>4</sub> <sup>2-</sup>	H <sub>2</sub> O	OH-

Species	Conjugate acid	Conjugate base
(i) NH <sub>3</sub>	NH <sup>†</sup>	$NH_2^-$
(ii) HCO <sub>3</sub>	$H_2CO_3$	CO <sub>3</sub> <sup>2-</sup>
(iii) HSO4	$H_2SO_4$	$SO_4^{2-}$
(iv) H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>	OH-
(v) CH <sub>3</sub> COOH	~ ~	CH <sub>3</sub> COO <sup>-</sup>
(vi) H <sub>2</sub> NCH <sub>2</sub> CO	ООН Н₃ЙСН₂СООН	
(vii) HS	$H_2S$	S <sup>2-</sup>
(viii) OH	H <sub>2</sub> O	O <sup>2-</sup>
	(i) NH <sub>3</sub> (ii) HCO <sub>3</sub> (iii) HSO <sub>4</sub> (iv) H <sub>2</sub> O (v) CH <sub>3</sub> COOH (vi) H <sub>2</sub> NCH <sub>2</sub> CO (vii) HS	(i) NH <sub>3</sub> NH <sub>4</sub> NH <sub>4</sub> (ii) HCO <sub>3</sub> H <sub>2</sub> CO <sub>3</sub> (iii) HSO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> (iv) H <sub>2</sub> O H <sub>3</sub> O <sup>+</sup> (v) CH <sub>3</sub> COOH CH <sub>3</sub> COOH <sub>2</sub> (vi) H <sub>2</sub> NCH <sub>2</sub> COOH H <sub>3</sub> NCH <sub>2</sub> COOI (vii) HS <sup>-</sup> H <sub>2</sub> S

8.	Lewis acid	Lewis base	
	(i) BF <sub>3</sub>	NH <sub>3</sub>	Lone pair donated by NH <sub>3</sub> and accepted by BF <sub>3</sub> .
	(ii) BeF <sub>2</sub>	F	Lone pair donated by F and accepted by BeF <sub>2</sub> .
	(iii) S	SO <sub>3</sub> <sup>2-</sup>	Lone pair donated by $SO_3^{2-}$ and accepted by S.
	(iv) SO <sub>3</sub>	(CH <sub>3</sub> ) <sub>3</sub> N	Lone pair donated by (CH <sub>3</sub> )N and accepted by SO <sub>3</sub> .
	(v) Fe <sup>2+</sup>	CNT	Lone pair donated by CN and accepted by Fe <sup>2+</sup> .
	(vi) CO <sub>2</sub>	OH_	Lone pair donated by OH and accepted by CO <sub>2</sub> .

- 9.  $C_2H_3O^-$ ,  $SO_3^{2-}$  and  $F^-$  These are conjugate of weak acids, (a) (c) (d) hence their aqueous solutions are alkaline.
  - (b) Na<sup>+</sup> - It is a conjugate of a strong alkali, hence the aqueous solution is neutral.
  - (e) NH<sub>4</sub> - It is a conjugate of a weak base, hence its aqueous solution is acidic.
  - (f) AlCl<sub>3</sub> - [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> is a conjugate of a weak base, hence its aqueous solution is acidic.

$$[AI(H_2O)_6]^{3+} + H_2O \iff [AI(H_2O)_5(OH)]^{2+} + H_3O^+$$

- 10. (a)  $[Fe(H_2O)_6]^{3+}$  Small radii and higher charge increases acid strength.
  - (b) [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> Smaller size of Al<sup>3+</sup> than Ga<sup>3+</sup>.
  - (c) Si(OH)<sub>4</sub> Smaller size of Si than Ge.
  - (d) HClO<sub>4</sub> More electronegative oxygen atoms with Cl than in HClO3 or formal charge is more on Cl in HClO4 than in HClO<sub>3</sub>.
  - (e) HMnO<sub>4</sub> Higher oxidation number of Mn.
  - (f) H<sub>2</sub>SO<sub>4</sub> Higher electronegativity of S.
- 11. (i) Acidic, (ii) Alkaline, (iii) one proton, (iv) non-aqueous solutions, (v) an electron pair acceptor, (vi) an electron pair donor, (vii) Lewis bases, (viii) A Bronsted acid, (ix) Weak base, (x) Neutralisation.
- 12. (a) HF < HCl < HBr < HI
  - (b) HClO < HClO<sub>2</sub> < HClO<sub>3</sub> < HClO<sub>4</sub>
  - (c)  $H_2O < CH_3OH < OH^- < CH_3O^-$
  - (d)  $SiO_2 < CO_2 < N_2O_5 < SO_3$
  - (e)  $ClO_4^- < ClO_3^- < ClO_2^- < ClO_3^-$
  - (f)  $[Na(H_2O)_n]^+ < [Ca(H_2O)_n]^{2+} < [Al(H_2O)_6]^{3+} < [Fe(H_2O)_6]^{3+}$
  - (g)  $F^- < OH^- < NH_2^- < CH_3^-$
  - (h)  $CH_4 < NH_3 < H_2O < HF$
  - (i)  $H_3O^+ < H_2O < OH^-$
  - (j)  $CH_3F < CH_3OH < CH_3NH_2$
- 13. (a) The reaction moves from left to right as HNO2 is stronger than HCN, i.e., it is a better proton donor.
  - (b) HF is a strong acid than H2O. The reaction moves from right to left.
  - (c) The reaction moves from right to left as Na<sup>+</sup> is a very weak acid while NaOH is a strong alkali.

#### **Answers**: Matching Type Questions

(a-vii); (b-v); (c-viii); (d-i); (e-iii); (f-iv); (g-ii); (h-vi).

# ILLUSTRATIONS OF OBJECTIVE QUESTIONS



- 1. Boric acid is a weak Lewis acid. When it is dissolved in water, the aqueous solution contains ions:
  - (a)  $H_3BO_3 \rightleftharpoons H_2BO_3 + H^+$
  - (b)  $H_3BO_3 + H_2O \Longrightarrow B(OH)_4^- + H^+$
  - (c)  $H_3BO_3 \rightleftharpoons HBO_3^{2-} + 2H^+$
  - (d)  $H_3BO_3 \implies BO_3^{3-} + 3H^+$

Ans. (b)

[Hint: B(OH)<sub>3</sub>, i.e., H<sub>3</sub>BO<sub>3</sub> in aqueous medium coordinates with a molecule of water to form a hydrated species, H O→ B(OH)<sub>3</sub>. B<sup>3+</sup> ion pulls the σ-electron charge of the coordinated O-atom towards itself. The coordinated oxygen, in turn, pulls the σ-electron charge of the O→H bond of the attached water molecule towards itself. This facilitates the removal of proton ion from the O→H bond.]

- 2. Which is the correct trend of the acid strength?
  - (a)  $HClO_4 > HClO_3 > HClO_2$
  - (b)  $H_3PO_4 > H_3PO_3 > H_3PO_2$
  - (c) HF > HCl > HBr
  - (d) HC1 > HF > H<sub>2</sub>S

**Ans.** (a, d)

[Hint: (a) The number of electronegative atoms with central atom increases.

- (b) All the three have nearly same acid strength.
- (c) Acid strength increases in the hydrides in a group, if size of the central atom increases.
- (d) HCl is stronger than HF and HF is stronger than H2S.]
- 3. In  $I_3$ , Lewis base is:
  - (a) I<sub>2</sub>

(b) I<sub>2</sub><sup>+</sup>

(c)  $I_{2}^{-}$ 

(d) I

- Ans. (d)
- [Hint:  $I_2 + \Gamma \longrightarrow I_3^-$ ]

Acid Base

- 4. AlCl<sub>3</sub> acts as an acid according to the concept of:
  - (a) Bronsted-Lowry
- (b) Arrhenius
- (c) Lewis
- (d) all of these

Ans. (c)

[Hint: Al in AlCl<sub>3</sub> is electron deficient. It can accept an electron pair.]

- 5. The conjugate base of NH<sub>3</sub> is:
  - (a) NH<sub>4</sub>
- (b)  $NH_2^-$
- (c) NH<sup>2-</sup>

(d) NH2OH

Ans. (b)

[Hint:  $NH_3 \rightleftharpoons NH_2^- + H^+$ ]

Acid Base

- 6. 1 mole of H<sub>3</sub>PO<sub>3</sub> is neutralised by.....mole/s of NaOH:
  - (a) 6 Ans. (c)
- (b) 3
- (c) 2
- (d) 1

**[Hint**:  $H_3PO_3$  is a dibasic acid.  $H_3PO_3 \rightleftharpoons 2H^+ + HPO_3^{2-}$ ]

7. Consider the following Lewis acid-base reaction,

$$SnCl_4 + 2Cl^- \longrightarrow SnCl_6^2$$
Acid

Hybridization of Sn in SnCl<sub>4</sub> and SnCl<sub>6</sub><sup>2-</sup> are respectively:

- (a)  $sp^3$ ,  $sp^3d^2$
- (b)  $dsp^2$  to  $sp^3d^2$
- (c)  $sp^3$ ,  $sp^3d^3$
- (d)  $sp^3$  to  $d^2sp^3$

Ans. (a)

- 8. Which of the following statements is incorrect?
  - (a) Liquid ammonia like water is an amphiprotic.
  - (b) In the equation,  $Ag^+ + 2CN^- \longrightarrow [Ag(CN)_2]^-$ ,  $Ag^+$  ion acts as a Lewis acid.
  - (c) I<sup>−</sup> ion is a Lewis as well as Bronsted base.
  - (d) BF3 is a Lewis as well as Bronsted acid.

Ans. (d

[Hint : (a)  $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ Acid Base Acid Base

- (b) Ag<sup>+</sup> acts as a Lewis acid as it accepts lone pairs of electrons from CN<sup>-</sup> ions.
- (c) I<sup>-</sup> ion contains lone pair of electrons which it can donate, hence it can act as a Lewis base. I<sup>-</sup> can accept proton, hence it acts as a Bronsted base.
- (d) BF<sub>3</sub> acts as a Lewis acid as it is an electron pair acceptor but it has no tendency to lose a proton, hence it is not a Bronsted acid.]
- 9. Given,

Acid

- $pK_a$ (i)
- (A) CH<sub>3</sub>CO<sub>2</sub>H (B) CCl<sub>3</sub>CO<sub>2</sub>H
- (i) 0.7 (ii) 0.2
- (C) CICH<sub>2</sub>CO<sub>2</sub>H
- (iii) 4.8
- (D) F<sub>3</sub>CCO<sub>2</sub>H
- (iv) 2.9

The correct code is:

A B C D

- (a) (iii) (i) (iv) (ii) (b) (ii) (iv) (i) (iii)
- (c) (iii) (ii) (i) (iv)
- (d) (i) (iii) (ii) (iv)
- Ans. (a)

**[Hint:** Smaller the value of the  $pK_a$  indicates the stronger acid.]

- 10. Which of the following represent conjugate acid-base pairs?
  - (a) H<sub>2</sub>O, H<sub>3</sub>O<sup>+</sup>
- (b) OH<sup>-</sup>, HNO<sub>3</sub>
- (c) H<sub>2</sub>SO<sub>4</sub>, SO<sub>4</sub><sup>2-</sup>
- (d) HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

Ans. (a, d)

lHint: The conjugate acid-base pairs differ by H+.

$$\begin{pmatrix} H_2O & H_3O^+ \\ Base & Acid \end{pmatrix}; \; \begin{pmatrix} HC_2H_3O_2 & C_2H_3O_2^- \\ Acid & Base \end{pmatrix} J$$

# **OBJECTIVE QUESTIONS**

7		· .	

Tat.	e: Choose the correct answer out of given altern	ativo	e in each assection	
		auve		_
	Acids are the substances that yield H <sup>+</sup> ions in aqueous			
	solutions while bases yield OH <sup>-</sup> ions. In a neutral solution:		(6) 112004	
	(a) There are no H <sup>+</sup> ions	15.	Which of the following is a soft acid according to Pearson	ı's
	(b) There are no OH <sup>-</sup> ions	٠,	concept ?	
	(c) There are neither H <sup>+</sup> nor OH <sup>-</sup> ions		(a) $Ag^+$	
	(d) H <sup>+</sup> and OH <sup>-</sup> ions are present in very small but equal in		(c) $A1^{3+}$	
	number	16.	The conjugate acid of HPO <sub>4</sub> <sup>2-</sup> is:	
	Which of the following is a weakest base?			
	(a) NaOH $\Box$ (b) $Zn(OH)_2$ $\Box$	٠,	2	
	(c) KOH $\Box$ (d) Ca(OH) <sub>2</sub> $\Box$	17		_
	Which of the following represents acid-base pair for the	. 17.	Which of the following is a Lewis base?	
	equilibrium reaction,		(-,	
	$HCl + H_2O \Longrightarrow H_3O^+ + Cl^-$ ?			
	(a) HCl, $H_2O$ $\Box$ (b) HCl, $H_3O^+$ $\Box$	18.	In the reaction,	
	(c) HCl, Cl <sup>-</sup> $\square$ (d) Cl <sup>-</sup> , H <sub>2</sub> O $\square$		$BCl_3 + PH_3 \rightarrow Cl_3B \leftarrow PH_3$ , Lewis base is :	
4.	The conjugate acid of $S_2O_8^{2-}$ is :		(a) $BCl_3$	
	(a) $HS_2O_8^-$		(c) Cl <sub>3</sub> B—PH <sub>3</sub>	
	(c) $H_2SO_4$ $\square$ (d) $H_2S_2O_3$ $\square$	19.	In the reaction,	
5.	The conjugate base of $H_2PO_4^-$ is : [C.E.T. (Karnataka) 2008]		$HC_2O_4^- + PO_4^{3-} \iff HPO_4^{2-} + C_2O_4^{2-}$	
	(a) $H_3PO_4$		which are the two Bronsted bases ?	
	(c) $PO_4^{3-}$ $\square$ (d) $H_3PO_3$ $\square$			_
6. ·	Which of the following is a Lewis acid?		2 0	
	(a) $NH_3$ $\square$ (b) $H_2SO_4$ $\square$			
	(c) $H_3\overset{+}{O}$ $\Box$ (d) $AlCl_3$	20.	The conjugate acid of NH <sub>2</sub> is:	
7	BF <sub>3</sub> is taken as an example of Lewis acid because it behaves:		(a) $NH_3$ $\Box$ (b) $NH_2OH$	
′.	(a) electrophile $\Box$ (b) nucleophile $\Box$		(c) $NH_4^+$ $\square$ (d) $N_2H_4$	
	(c) neutral molecule	21.	The strongest Bronsted base in the following anion is:	
8	The strongest acid of the following is:		(a) $ClO^-$	
0.	(a) HCl			
	(c) $HClO_4$ $\Box$ (d) $H_3PO_4$ $\Box$	22.	The strongest Lewis base among the following is:	
Q	Which of the following is the Bronsted acid?		(a) OH	
٠.	(a) Cl		· -	
	(c) HCOO	200	•	ш
10	The reaction of water with ammonia is given by the	23.	Which of the following is a Lewis acid?	_
10.	following equation,		(a) $PCl_5$ $\square$ (b) $NCl_3$	Ш
	H <sub>2</sub> O + NH <sub>3</sub> $\rightleftharpoons$ NH <sub>4</sub> <sup>+</sup> + OH <sup>-</sup>			
	in this reaction water behaves as:	24.	The following equilibrium is established when HCl	is
	(a) neutral		dissolved the acetic acid,	
	the state of the s		$HCI + CH_3COOH \rightleftharpoons CI^- + CH_3COOH_2^+$	
11.			the set that characterises the conjugate acid-base pairs is	3:
11.	The compound that is not a Lewis acid is:		(a) (HCl, CH <sub>3</sub> COOH) and (Cl <sup>-</sup> , CH <sub>3</sub> COOH <sub>2</sub> <sup>+</sup> )	
·	(a) $BF_3$ $\square$ (b) $BaCl_2$ $\square$ (c) $AlCl_2$ $\square$ (d) $SnCl_4$ $\square$		(b) (HCl, CH <sub>3</sub> COOH <sub>2</sub> ) and (CH <sub>3</sub> COOH, Cl <sup>-</sup> )	
10	— · · · · · · · · · · · · · · · · · · ·		(c) $(CH_3COOH_2^+, HCI)$ and $(CI^-, CH_3COOH)$	
12.	Weakest acid of the following is:	,	(d) (HCl, Cl <sup>-</sup> ) and (CH <sub>3</sub> COOH <sub>2</sub> , CH <sub>3</sub> COOH)	
	(a) ClO <sub>3</sub> (OH)	25		ш
12	(c) SO(OH) <sub>2</sub>	25.		
13.	Ionic theory of acids and bases was proposed by:		OH <sup>-</sup> , NH <sub>2</sub> , H—C $\equiv$ C <sup>-</sup> and CH <sub>3</sub> —CH <sub>2</sub> ?	
	(a) Lowry		(a) $CH_3 - CH_2^- > NH_2^- > H - C = C^- > OH^-$	
14	(c) Lewis		(b) $H-C \equiv C^- > CH_3-CH_2^- > NH_2^- > OH^-$	
14.	Which of the following can act as both a Bronsted acid and		(c) $OH^- > NH_2^- > HC \equiv C^- > CH_3CH_2^-$	
	a Bronsted base ?		(d) $NH_2^- > H - C = C^- > OH^- > CH_3 - CH_2^-$	

26.	Which is the weakest base among the following?	39.	For HCl + CH <sub>3</sub> COOH system, acetic acid serve	
	(a) $C1^-$		(a) protophilic solvent   (b) protogenic so	olvent 🗆
	(c) $Br^ \square$ (d) $F^-$	,	(c) aprotic solvent $\Box$ (d) none of these	. 🗖
27.	Among the trihalides of nitrogen, which one is the least	40.	Ampholyte is:	•
	basic?		(a) $H_2O$	
	(a) $NI_3$ $\Box$ (b) $NBr_3$ $\Box$		(c) $H_2NCH_2COOH$ $\Box$ (d) all of these	
	(c) $NCl_3$ $\square$ (d) $NF_3$ $\square$	41.	A reaction between AlCl <sub>3</sub> and NH <sub>3</sub> is called:	
28.	In which of the following cases the acid strength is highest?		(a) addition   (b) substitution	· 🗆
	(a) $pK_a = 5$		(c) neutralisation	. 🗆
	(c) $K_a = 10^{-6}$	42.	Which of the following gases on dissolution in	water make
29.	Dissociation of H <sub>3</sub> PO <sub>3</sub> occurs in stages.		the solution acidic ?	
	(a) 1		(A) CO, (B) CO <sub>2</sub> , (C) SO <sub>3</sub> and (D) PH <sub>3</sub>	
	(c) 3	-	(a) (A) and (B) $\square$ (b) (B) and (C)	
30.	The strength of the acid depends on the :		(c) (C) and (D) $\square$ (d) (B) and (D)	
00.	(a) number of hydrogen atoms present in the molecule □	13	Acid strength of the weak acids $HA_1$ , $HA_2$ and	
		40.		This can be
		1	written as,	
	(c) oxygen content		$HA_1 < HA_2$ and $HA_3 < HA_1$	
	(d) concentration of hydrogen ions furnished by ionisation		the correct order of strength of the conjugate b	ases would
			be:	
31.	The dissociation constants of acids $HA$ , $HB_r$ $HC$ and $HD$		(a) $A_3^- > A_1^- > A_2^-$	
	are $3 \times 10^{-5}$ , $5 \times 10^{-9}$ , $1 \times 10^{-2}$ and $7 \times 10^{-5}$ respectively. The		(c) $A_1^- = A_3^- < A_2^-$ (d) none of these	
	weakest acid is:	44.	* *	orkee 1991]
	(a) $HD$ $\square$ (b) $HA$ $\square$		(a) $H_2CO_3$ and $HCO_3$ $\square$ (b) $H_2CO_3$ and $H_2CO_3$ $\square$	
	(c) $HB$ $\square$ (d) $HC$ $\square$		(c) $CO_3^{2-}$ and $H_3O^+$	<sub>2</sub> O
32.	On the basis of acid-base concept, the redox reactions	45.	For the reaction,	
	are also considered as acid-base reaction.		$NH_4^+ + S^{2-} \longrightarrow NH_3 + HS^-,$	
	(a) Arrhenius $\Box$ (b) Lewis $\Box$		$NH_3$ and $S^{2-}$ are a group of :	
	(c) Usanovich $\Box$ (d) Bronsted-Lowry $\Box$		(a) bases	
33.	The concept that acid is proton donor and base is proton		(b) acids	
	acceptor was given by :		(c) conjugate pair of acid and base	
*	(a) Arrhenius $\Box$ (b) Bronsted-Lowry $\Box$		(d) none of the above	
	(c) Lewis	46.	HNO <sub>3</sub> and HF both are acids. But when HNO <sub>3</sub>	dissolves in
34.	According to Lewis concept, the acid is:		HF, it behaves as :	
	(a) proton acceptor $\Box$ (b) electron-pair donor $\Box$		(a) an acid	
	(c) electron pair acceptor □ (d) proton donor □		(c) a Zwitter ion   (d) amphiprotic	solvent $\square$
35.	According to the Lewis acid-base concept:	47.	Which of the following is not a Lewis acid?	
	(a) molecule in which all atoms have their octets is an acid		•	(M.P.) 2002]
			(a) CO	
	(b) negatively charged ions are acids		(c) $SO_3$	
	(c) all positively charged ions are not acids	48.		
	(d) molecule in which a central atom has available <i>d</i> -orbital	10.	•	.E.E.E. 2002]
	to accommodate electron pair is an acid		(a) $HSO_4^-$	
36.	Which of the following is a Lewis base?	ļ	(c) $NH_3$ $\square$ (d) $OH^-$	
	(a) $CH_3NH_2$	10	In the equation : $I_2 + I^- \longrightarrow I_3$ , which is the I	
	2	49.		(Raj.) 2002]
. 27		. }		
37.	According to Lowry-Bronsted concept, the relative strength		(a) I <sub>2</sub>	
	of the bases CH <sub>3</sub> COO <sup>-</sup> , OH <sup>-</sup> and Cl <sup>-</sup> follows the order:		(c) $I_3$	e 🗆
	(a) CH <sub>3</sub> COO <sup>-</sup> > OH <sup>-</sup> > CI <sup>-</sup>	50.		
	(b) OH <sup>-</sup> > CH <sub>3</sub> COO <sup>-</sup> > Cl <sup>-</sup>		(a) H <sub>3</sub> O, HPO <sub>2</sub> <sup>2</sup> , HCO <sub>3</sub>	
	(c) CH <sub>3</sub> COO <sup>-</sup> > CI <sup>-</sup> > OH <sup>-</sup>		(b) H <sub>2</sub> O, HPO <sub>3</sub> <sup>2</sup> , H <sub>2</sub> PO <sub>2</sub> <sup>2</sup>	
	(d) $OH^- > CI^- > CH_3COO^-$		(c) $HSO_4$ , $H_2PO_4$ , $H_2PO_3$	. 🖳
38.	ĕ		(d) All of these	
	Bronsted acid?	51.	Which does not react with NaOH?	
	(a) HCl $\Box$ (b) H <sub>2</sub> SO <sub>4</sub> $\Box$		(a) $NaH_2PO_2$	
	(c) $HSO_3^ \Box$ (d) $SO_3$ $\Box$		(c) $Na_2HPO_2$ $\Box$ (d) $NaHCO_3$	. 0

52.	$[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \longrightarrow [Cu(H_2O)_4]^{2+}$		(a) (iii) $<$ (i) $<$ (iv) $<$ (ii) $\square$ (b) (iv) $<$ (ii) $<$ (iii) $<$ (i)	
	$A_1$ $A_2$ $A_3$		(c) (ii) $<$ (iii) $<$ (i) $<$ (iv) $\Box$ (d) (i) $<$ (iii) $<$ (ii) $<$ (iv)	
	+ $[Al(H_2O)_5(OH)]^{2+}$	64.	$H_3PO_3$ has non-ionisable P—H bond or bonds.	
	$A_4$		[J.E.E. (Orissa) 2	2008]
	(a) $A_1$ is an acid and $A_2$ is a base		(a) none	
	(b) $A_1$ is a base and $A_2$ is an acid		(c) 2	
	(c) $A_3$ is conjugate acid of $A_1$ and $A_4$ is conjugate base of	65.	Which is tribasic acid? [B.C.E.C.E. 2	2008]
	$A_2$		(a) $H_3PO_2$	
	(d) $A_3$ is conjugate base of $A_1$ and $A_4$ is conjugate acid of		(c) $H_4P_2O_7$	
	$A_2$	66.	Identify Bronsted-Lowry acids in the reaction given :	
53.	Water is a : [K.C.E.T. 2002]		$[Al(H_2O)_6]^{3+} + HCO_3^- \longrightarrow [Al(H_2O)_5(OH^-)]^{2+} + H_2CO$	)_
00.	(a) protophobic solvent $\square$ (b) protophilic solvent $\square$		$\begin{array}{cccc} (A) & (B) & (C) & (D) \end{array}$	3
	(c) amphiprotic solvent (d) aprotic solvent (		The correct answer is: [E.A.M.C.E.T. (Med.) 2	2008]
54.	Ammonium ion is: [K.C.E.T. 2002]		(a) (A), (C)	
V 2.	(a) a conjugate acid		(c) $(A)$ , $(D)$ $\Box$ (d) $(B)$ , $(C)$	
	(b) a conjugate base	67.	Which is correct trend of the acid strength?	
	(c) neither an acid nor a base		(a) $H_2S > H_2O > HF$	
	(d) both an acid and a base		(b) HClO <sub>4</sub> > HClO <sub>3</sub> > HClO <sub>2</sub>	
55	H <sub>3</sub> PO <sub>3</sub> phosphorus acid is : [P.M.T. (Kerala) 2003]		(c) $H_3PO_4 > H_3PO_3 > H_3PO_2$	
50.	(a) diprotic acid		(d) $HNO_2 > HNO_3 > H_2N_2O_2$	
	(c) monoprotic acid	68.	The order of Lewis acid strength is:	
56	Arrange NH $_{+}^{4}$ , H $_{2}^{2}$ O, H $_{3}^{+}$ O, HF and OH $_{-}^{-}$ in increasing order		(a) $BBr_3 > BCl_3 > BF_3$ $\square$ (b) $BCl_3 > BBr_3 > BF_3$	
00.	of acidic nature : [B.V. (Pune) 2003]		(c) $BF_3 > BCl_3 > BBr_3$ $\square$ (d) $BCl_3 > BrF_3 > BBr_3$	
	(a) $H_3O^+ < NH_4^+ < HF < OH^- < H_2O$	69.	The increasing order of acidity of H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> O and CO	b is:
	(b) $NH_4^+ < HF < H_3O^+ < H_2O < OH^-$		(a) $H_2O_2 > H_2O > CO_2$ (b) $H_2O_2 > CO_2 > H_2O$	
	(c) $OH^- < H_2O < NH_4^+ < HF < H_3O^+$		(c) $H_2O > H_2O_2 > CO_2$	
	(d) $H_3O^+ > HF > H_2O > NH_4^+ > OH^-$	`70.	The true statement for the acids of phosphorus, H <sub>3</sub>	2PO2,
57	Which among the following is amphoteric oxide?		H <sub>3</sub> PO <sub>3</sub> and H <sub>3</sub> PO <sub>4</sub> is:	
<b>.</b> .		i	(a) all of them are reducing agents	
	1A.I.E.E.E. 20031	l	(a) an or them are reducing agents	_
	[A.I.E.E.E. 2003] (a) ZnO		(b) all of them are tribasic acids	
	(a) $ZnO$ $\Box$ (b) $Na_2O$ $\Box$		(b) all of them are tribasic acids	
58.	(a) ZnO $\Box$ (b) Na <sub>2</sub> O $\Box$ (c) SO <sub>2</sub> $\Box$ (d) B <sub>2</sub> O <sub>3</sub> $\Box$			
58.	(a) ZnO $\Box$ (b) Na <sub>2</sub> O $\Box$ (c) SO <sub>2</sub> $\Box$ (d) B <sub>2</sub> O <sub>3</sub> $\Box$ Which of the given hydride of the nitrogen is acidic in	,	<ul><li>(b) all of them are tribasic acids</li><li>(c) the geometry of phosphorus is tetrahedral in all</li></ul>	
58.	(a) ZnO $\Box$ (b) Na <sub>2</sub> O $\Box$ (c) SO <sub>2</sub> $\Box$ (d) B <sub>2</sub> O <sub>3</sub> $\Box$ Which of the given hydride of the nitrogen is acidic in nature? [P.M.E.T. 2003]	71.	<ul><li>(b) all of them are tribasic acids</li><li>(c) the geometry of phosphorus is tetrahedral in all three</li></ul>	□ l the □
58.	(a) ZnO $\square$ (b) Na <sub>2</sub> O $\square$ (c) SO <sub>2</sub> $\square$ (d) B <sub>2</sub> O <sub>3</sub> $\square$ Which of the given hydride of the nitrogen is acidic in nature? [P.M.E.T. 2003] (a) NH <sub>3</sub> $\square$ (b) N <sub>3</sub> H $\square$	71.	<ul> <li>(b) all of them are tribasic acids</li> <li>(c) the geometry of phosphorus is tetrahedral in all three</li> <li>(d) the order of acidity is H<sub>3</sub>PO<sub>4</sub> &gt; H<sub>3</sub>PO<sub>3</sub> &gt; H<sub>3</sub>PO<sub>2</sub></li> </ul>	l the
	(a) ZnO $\Box$ (b) Na <sub>2</sub> O $\Box$ (c) SO <sub>2</sub> $\Box$ (d) B <sub>2</sub> O <sub>3</sub> $\Box$ Which of the given hydride of the nitrogen is acidic in nature? [P.M.E.T. 2003] (a) NH <sub>3</sub> $\Box$ (b) N <sub>3</sub> H $\Box$ (c) N <sub>2</sub> H <sub>4</sub> $\Box$ (d) All of these $\Box$	71.	<ul> <li>(b) all of them are tribasic acids</li> <li>(c) the geometry of phosphorus is tetrahedral in all three</li> <li>(d) the order of acidity is H<sub>3</sub>PO<sub>4</sub> &gt; H<sub>3</sub>PO<sub>3</sub> &gt; H<sub>3</sub>PO<sub>2</sub></li> <li>Of the following acids, the one which has the capability</li> </ul>	l the
	(a) ZnO $\square$ (b) Na <sub>2</sub> O $\square$ (c) SO <sub>2</sub> $\square$ (d) B <sub>2</sub> O <sub>3</sub> $\square$ Which of the given hydride of the nitrogen is acidic in nature? [P.M.E.T. 2003] (a) NH <sub>3</sub> $\square$ (b) N <sub>3</sub> H $\square$ (c) N <sub>2</sub> H <sub>4</sub> $\square$ (d) All of these $\square$ A group of acidic oxide is : [P.E.T. (M.P.) 2003]	71.	<ul> <li>(b) all of them are tribasic acids</li> <li>(c) the geometry of phosphorus is tetrahedral in all three</li> <li>(d) the order of acidity is H<sub>3</sub>PO<sub>4</sub> &gt; H<sub>3</sub>PO<sub>3</sub> &gt; H<sub>3</sub>PO<sub>2</sub></li> <li>Of the following acids, the one which has the capability form complex compounds and also possesses oxidising</li> </ul>	l the
	(a) ZnO $\square$ (b) Na <sub>2</sub> O $\square$ (c) SO <sub>2</sub> $\square$ (d) B <sub>2</sub> O <sub>3</sub> $\square$ Which of the given hydride of the nitrogen is acidic in nature? [P.M.E.T. 2003] (a) NH <sub>3</sub> $\square$ (b) N <sub>3</sub> H $\square$ (c) N <sub>2</sub> H <sub>4</sub> $\square$ (d) All of these $\square$ A group of acidic oxide is : [P.E.T. (M.P.) 2003] (a) CrO <sub>3</sub> , Mn <sub>2</sub> O <sub>7</sub> $\square$ (b) ZnO, Al <sub>2</sub> O <sub>3</sub> $\square$	71.	<ul> <li>(b) all of them are tribasic acids</li> <li>(c) the geometry of phosphorus is tetrahedral in all three</li> <li>(d) the order of acidity is H<sub>3</sub>PO<sub>4</sub> &gt; H<sub>3</sub>PO<sub>3</sub> &gt; H<sub>3</sub>PO<sub>2</sub></li> <li>Of the following acids, the one which has the capabili form complex compounds and also possesses oxidising reducing properties is:</li> <li>[J.E.E. (W.B.)</li> </ul>	l the
59.	(a) $ZnO$	71.	<ul> <li>(b) all of them are tribasic acids</li> <li>(c) the geometry of phosphorus is tetrahedral in all three</li> <li>(d) the order of acidity is H<sub>3</sub>PO<sub>4</sub> &gt; H<sub>3</sub>PO<sub>3</sub> &gt; H<sub>3</sub>PO<sub>2</sub></li> <li>Of the following acids, the one which has the capabili form complex compounds and also possesses oxidising reducing properties is: <ul> <li>[J.E.E. (W.B.)</li> <li>(a) HNO<sub>3</sub></li> <li>(b) HNO<sub>2</sub></li> <li>(c) HCOOH</li> <li>(d) HCN</li> </ul> </li> </ul>	l the
59.	(a) ZnO $\square$ (b) Na <sub>2</sub> O $\square$ (c) SO <sub>2</sub> $\square$ (d) B <sub>2</sub> O <sub>3</sub> $\square$ Which of the given hydride of the nitrogen is acidic in nature? [P.M.E.T. 2003] (a) NH <sub>3</sub> $\square$ (b) N <sub>3</sub> H $\square$ (c) N <sub>2</sub> H <sub>4</sub> $\square$ (d) All of these $\square$ A group of acidic oxide is : [P.E.T. (M.P.) 2003] (a) CrO <sub>3</sub> , Mn <sub>2</sub> O <sub>7</sub> $\square$ (b) ZnO, Al <sub>2</sub> O <sub>3</sub> $\square$		<ul> <li>(b) all of them are tribasic acids</li> <li>(c) the geometry of phosphorus is tetrahedral in all three</li> <li>(d) the order of acidity is H<sub>3</sub>PO<sub>4</sub> &gt; H<sub>3</sub>PO<sub>3</sub> &gt; H<sub>3</sub>PO<sub>2</sub></li> <li>Of the following acids, the one which has the capabili form complex compounds and also possesses oxidising reducing properties is: [J.E.E. (W.B.) 2</li> <li>(a) HNO<sub>3</sub> □ (b) HNO<sub>2</sub></li> <li>(c) HCOOH □ (d) HCN</li> <li>Three reactions involving H<sub>2</sub>PO<sub>4</sub> are given below :</li> </ul>	l the
59.	(a) ZnO		<ul> <li>(b) all of them are tribasic acids</li> <li>(c) the geometry of phosphorus is tetrahedral in all three</li> <li>(d) the order of acidity is H<sub>3</sub>PO<sub>4</sub> &gt; H<sub>3</sub>PO<sub>3</sub> &gt; H<sub>3</sub>PO<sub>2</sub></li> <li>Of the following acids, the one which has the capabili form complex compounds and also possesses oxidising reducing properties is : [J.E.E. (W.B.) 2</li> <li>(a) HNO<sub>3</sub> □ (b) HNO<sub>2</sub></li> <li>(c) HCOOH □ (d) HCN</li> <li>Three reactions involving H<sub>2</sub>PO<sub>4</sub> are given below :</li> <li>(i) H<sub>3</sub>PO<sub>4</sub> + H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup> + H<sub>2</sub>PO<sub>4</sub></li> </ul>	l the
59.	(a) ZnO		<ul> <li>(b) all of them are tribasic acids</li> <li>(c) the geometry of phosphorus is tetrahedral in all three</li> <li>(d) the order of acidity is H<sub>3</sub>PO<sub>4</sub> &gt; H<sub>3</sub>PO<sub>3</sub> &gt; H<sub>3</sub>PO<sub>2</sub></li> <li>Of the following acids, the one which has the capabili form complex compounds and also possesses oxidising reducing properties is: [J.E.E. (W.B.) 2</li> <li>(a) HNO<sub>3</sub> □ (b) HNO<sub>2</sub></li> <li>(c) HCOOH □ (d) HCN</li> <li>Three reactions involving H<sub>2</sub>PO<sub>4</sub> are given below:</li> <li>(i) H<sub>3</sub>PO<sub>4</sub> + H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup> + H<sub>2</sub>PO<sub>4</sub> (ii) H<sub>2</sub>PO<sub>4</sub> + H<sub>2</sub>O → HPO<sub>4</sub><sup>2</sup> + H<sub>3</sub>O<sup>+</sup></li> </ul>	l the
59. 60.	(a) ZnO		<ul> <li>(b) all of them are tribasic acids</li> <li>(c) the geometry of phosphorus is tetrahedral in all three</li> <li>(d) the order of acidity is H<sub>3</sub>PO<sub>4</sub> &gt; H<sub>3</sub>PO<sub>3</sub> &gt; H<sub>3</sub>PO<sub>2</sub></li> <li>Of the following acids, the one which has the capabili form complex compounds and also possesses oxidising reducing properties is: [J.E.E. (W.B.) : (a) HNO<sub>3</sub> ☐ (b) HNO<sub>2</sub></li> <li>(c) HCOOH ☐ (d) HCN</li> <li>Three reactions involving H<sub>2</sub>PO<sub>4</sub> are given below :</li> <li>(i) H<sub>3</sub>PO<sub>4</sub> + H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup> + H<sub>2</sub>PO<sub>4</sub></li> <li>(ii) H<sub>2</sub>PO<sub>4</sub> + H<sub>2</sub>O → HPO<sub>4</sub><sup>2-</sup> + H<sub>3</sub>O<sup>+</sup></li> <li>(iii) H<sub>2</sub>PO<sub>4</sub> + OH → H<sub>3</sub>PO<sub>4</sub> + O<sup>2-</sup></li> </ul>	l the
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59. 60.	(a) ZnO	72.	<ul> <li>(b) all of them are tribasic acids</li> <li>(c) the geometry of phosphorus is tetrahedral in all three</li> <li>(d) the order of acidity is H<sub>3</sub>PO<sub>4</sub> &gt; H<sub>3</sub>PO<sub>3</sub> &gt; H<sub>3</sub>PO<sub>2</sub></li> <li>Of the following acids, the one which has the capabili form complex compounds and also possesses oxidising reducing properties is: [J.E.E. (W.B.) 2</li> <li>(a) HNO<sub>3</sub></li></ul>	
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<ul><li>59.</li><li>60.</li><li>61.</li></ul>	(a) ZnO	72. 73.	<ul> <li>(b) all of them are tribasic acids</li> <li>(c) the geometry of phosphorus is tetrahedral in all three</li> <li>(d) the order of acidity is H<sub>3</sub>PO<sub>4</sub> &gt; H<sub>3</sub>PO<sub>3</sub> &gt; H<sub>3</sub>PO<sub>2</sub></li> <li>Of the following acids, the one which has the capabili form complex compounds and also possesses oxidising reducing properties is: <ul> <li>[J.E.E. (W.B.)</li> <li>(a) HNO<sub>3</sub></li> <li>(b) HNO<sub>2</sub></li> </ul> </li> <li>(c) HCOOH</li> <li>(d) HCN</li> <li>Three reactions involving H<sub>2</sub>PO<sub>4</sub> are given below: <ul> <li>(i) H<sub>3</sub>PO<sub>4</sub> + H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup> + H<sub>2</sub>PO<sub>4</sub></li> <li>(ii) H<sub>2</sub>PO<sub>4</sub> + H<sub>2</sub>O → HPO<sub>4</sub><sup>2</sup> + H<sub>3</sub>O<sup>+</sup></li> <li>(iii) H<sub>2</sub>PO<sub>4</sub> + OH → H<sub>3</sub>PO<sub>4</sub> + O<sup>2</sup></li> </ul> </li> <li>In which of the above does H<sub>2</sub>PO<sub>4</sub> act as an acid? <ul> <li>[A.I.E.E.E.</li> </ul> </li> <li>(a) (i) only</li> <li>(b) (ii) only</li> <li>(c) (i) and (ii) only</li> <li>Pair of amphoteric species is:</li> <li>(a) H<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>O</li> <li>(b) HCO<sub>3</sub> and H<sub>2</sub>O</li> <li>(c) H<sub>2</sub>CO<sub>3</sub> and HCO<sub>3</sub></li> <li>(d) CO<sub>3</sub><sup>2</sup> and H<sub>3</sub>O<sup>+</sup></li> </ul>	
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A	Insw	ers																	
1.	(d)	2.	(b)	3.	(c)	4.	(a)	5.	(b)	6.	(d)	7.	(a)	8.	(c)	9.	(b)	10.	(c)
11.	(b)	12.	(c)	13.	(d)	14.	(d)	15.	(a)	16.	(a)	17.	(a)	18.	(b)	19.	(c)	20.	(a)
21.	(a)	22.	(c)	23.	(d)	24.	(d)	25.	(a)	26.	(b)	27.	(d)	28.	(d)	29.	(b)	30.	(d)
31.	(c)	32.	(c)	33.	(b)	34.	(c)	35.	(d)	36.	(a)	37.	(b)	38.	(d)	39.	(a)	40.	(c)
41.	(c)	42.	(b)	43.	(a)	44.	(d)	45.	(a)	46.	(b)	47.	(a)	48.	(a)	49.	(b)	50.	(c)
51.	(a)	52.	(b, c)	53.	(c)	54.	(a)	55.	(a)	56.	(c)	57.	(a)	58.	(b)	59.	(a)	60.	(b)
61.	(a)	62.	(a)	63.	(d)	64.	(b)	65.	(b)	66.	(c)	67.	(b)	68.	(a)	69.	(d)	70.	(c)
71.	(b)	72.	(b)	73.	(b)	74.	(a)												

1.	In the reaction, $AlCl_3 + Cl^- = AlCl_4^-$ , $AlCl_3$ can be classified			6.	BF <sub>3</sub> is a:		
	as:				(a) Bronsted acid	☐ (b) Bronsted base	
	(a) an acid	☐ (b) a base			(c) Lewis acid	☐ (d) Lewis base	
	(c) a salt	☐ (d) none of these		7.	Which is correct trend of	of the acid strength?	
2.	Identify the species that is amphiprotic:				(a) $HClO_4 > HClO_3 > HClO_2$		
		☐ (b) H <sub>2</sub> PO <sub>4</sub>			(b) $H_3PO_4 > H_3PO_3 > H$		
	(c) NH <sub>4</sub> <sup>+</sup>				(c) HCl > HBr > HI	Q <u>2</u>	
	[Hint: $H_2PO_4^- + H_2O \longrightarrow H_3PO_4 + OH^-$ ;				(d) All are true		
	$H_2PO_4^- + H_2O \longrightarrow HPO_4^{2-} + H_3O^+.$			8.	Which of the following cannot act as a Bronsted base?		
3.	Consider the following Lewis acid-base reaction,			(a) HCO <sub>3</sub>	2		
	•	$Cl^- \longrightarrow AlCl_4^-$			(c) NH <sub>2</sub>	☐ (d) NH <sub>4</sub> <sup>+</sup>	
	Hybridization of Al in AlCl <sub>3</sub> and AlCl <sub>4</sub> are respectively:			9.	Which one of the following is most basic?		
	(a) $sp^3$ , $dsp^2$				(a) C1 <sup>-</sup>	(b) F	
	(c) $dsp^2$ , $sp^3d$	$\Box$ (d) $sp^2$ , $sp^3$			(c) I <sup>-</sup>	□ (d) Br <sup>-</sup>	
4.	In a mixture of concentrated H <sub>2</sub> SO <sub>4</sub> and HNO <sub>3</sub> , inter-				[Hint: The conjugate base of a weak acid is a strong base.]		
	mediate formed is:			10.	Which of the following statements is true?		
	(a) H <sub>2</sub> SO <sub>4</sub> <sup>+</sup>	П (b) SO <sup>2-</sup>			(a) $H_3PO_3$ is a stronger	•	
	(c) $H_2NO_3^-$					of HF is a stronger acid t	
	$[\text{Hint} : \text{H}_2\text{SO}_4 + \text{HNO}_3 \longrightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-]$				(b) The aqueous solution	of the 13 th stronger actor	
_					(a) HClO is a recolor.	acid than UCIO	
5.	HNO <sub>3</sub> can accept proton and thus, acts as Bronsted-Lowry						
	base in:				(d) HNO <sub>3</sub> is a stronger	acid than HNO <sub>2</sub>	
	(a) $H_2SO_4$	□ (b) HF					
	(c) both	☐ (d) none of these					
	[Hint: HF + HNO <sub>3</sub> $\longrightarrow$ H <sub>2</sub> NO <sub>3</sub> + F <sup>-</sup> ]						

3. (d)

4. (d)

5. (c)

6. (c)

7. (a)

8. (d)

9. (b)

10. (d)

Objective Questions for IIT ASPIRANTS

### Matrix Matching Questions for IIT Aspirants

1. Match List-II with List-II:

#### List-I

#### List-II

(a) HF

(p) Strongest acid

(b) HCl

(q) React with glass

(c) HBr

(r) Monobasic

(d) HI

- (s) Strongest reducing agent
- 2. Match the solvents in List-I with their classifications in List-II:

#### List-I

#### List-II

- (a) Benzene
- (p) Protogenic
- (b) Water
- (q) Protophilic
- (c) Liquid NH<sub>3</sub>
- (r) Amphiprotic
- (d)  $CS_2(l)$
- (s) Aprotonic
- 3. Match List-I with List-II:

#### List-I

#### List-II

(a) OH-

- (p) Conjugate acid of O<sup>2-</sup>
- (b) HClO<sub>4</sub>
- (q) Conjugate acid of H2O
- (c)  $H_3O^+$
- (r) Conjugate base of H2O

- (d) ClO<sub>4</sub> is weakest conjugate base of
- (s) Strongest Bronsted acid
- (e) CH<sub>4</sub>
- (t) Weakest Bronsted acid
- · Match List-I with List-II:

#### List-I

#### List-II

- (a) Molecules with empty
- (p) Lewis base
- d-orbital with the central atom
- (b) Molecules with incomplete (q) Electron pair acceptor
- octet (c) Multiple bonded
- (r) Lewis acid
- compounds like CO, NO (d) R— $NH_2$ , R—O—H
- (s) Electron pair donor
- 5. Match List-I with List-II:

#### List-I

#### List-II

- (a) Oxide ion donor
- (p) Acid-base equilibrium
- (b) CaO  $\rightleftharpoons$  Ca<sup>2+</sup> + O<sup>2-</sup> (c) SO<sub>3</sub>
- (r) Hard base

(d)  $CO_3^{2-}$ 

(s) Base (lux-flood)

(q) Acid (lux-flood)

- (a-q)
- (b-r)
- (c-r)
- (d-p, r, s)
- (d-s)
  - (d-s)
- 4. (a-q, r) (a-s)
- (b-q, r) (b-p)
- (c-p, s) (c-q, r)
- (d-p, s) (d-r, s)

- (a-s) (b-p, q, r) (b-s)(a-p, r)
- (c-q)(c-q)

- (e-t)

# **Assertion-Reason Type Questions**

The following questions consist of an Assertion (A) and Reason (R). Use the following key to choose the correct answer:

- (a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
- (c) If (A) is correct but (R) is incorrect.
- (d) If both (A) and (R) are incorrect.
- (e) If (A) is incorrect but (R) is correct.
- 1. (A) HClO<sub>4</sub> is stronger acid than HClO<sub>3</sub>.
  - (R) Oxidation state of Cl is + 8 in HClO<sub>4</sub> and in HClO<sub>3</sub> is
- 2. (A) BF<sub>3</sub> is a Lewis acid as well as Bronsted-Lowry acid.
  - (R) Any species which can accept a lone pair of electrons is a Lewis acid and the species that can lose a proton is Bronsted-Lowry acid.

- 3. (A) If a base is strong, its conjugate acid is weak.
  - (R) HA is a conjugate acid of the base A<sup>-</sup>.
- 4. (A)  $H_2PO_3^-$  is amphiprotic.
  - (R) H<sub>2</sub>PO<sub>3</sub> can act as an acid by losing a proton as well as a base by accepting a proton.
- 5. (A) pH of 10<sup>-9</sup> N HCl is 9.
  - (R) pH is defined as the negative logarithm of [H<sup>+</sup>].
- 6. (A) CaO donates oxide, hence it is a base and CO2 accepts an oxide, hence it is an acid. This is in accordance with Lux-Flood concept.
  - (R) Cu<sup>+</sup>, Ag<sup>+</sup>, Au<sup>+</sup>, etc., are soft acids while Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>+</sup>, etc., are hard acids.
- Molecular mass 7. (A) Equivalent mass of a base =

Acidity

(R) Acidity is the number of replaceable hydrogen atoms in one molecule of the base. [A.I.E.E.E. 2008]

- 1. (c)
- 2. (e)
- 3. (b)
- 4. (a)
- 5. (e)
- 6. (b)
- 7. (c)

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

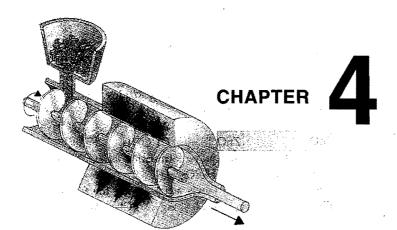
- 2. The total number of triprotic acids among the following is:  $H_3PO_4$ ,  $H_3PO_3$ ,  $H_3PO_2$ ,  $H_3BO_3$ ,  $H_4P_2O_7$
- 3. The total number of amphoteric oxides and hydroxides among the following is:

 $Na_2O$  CaO  $Al(OH)_3$   $Cr(OH)_3$  SnO ZnO  $Ca(OH)_2$   $Fe(OH)_3$ 

- **4.** Oxy acids in general can be formulated as  $XO_n(OH)_m$ . What is the value of 'm' in  $H_3PO_3$ ?
- 5. The total number of Lewis acids among the following is :  $BF_3$ ,  $H_2O$ ,  $NH_3$ ,  $AlCl_3$ ,  $Ag^+$ ,  $PCl_3$ , R— $NH_2$

### Answers

- 1. (6) Six out of the given acids are diprotic.  $H_2S_2O_7$ ,  $H_2SO_3$ ,  $H_2SO_4$ ,  $H_3PO_3$ ,  $H_2CO_3$ ,  $H_2CO_4$
- 2. (1) Only H<sub>3</sub>PO<sub>4</sub>
- 3. (4) SnO, ZnO, Al(OH)3 and Cr(OH)3 are amphoteric in nature.
- (2) H<sub>3</sub>PO<sub>3</sub> is diprotic. It has two —OH groups. It is represented as HPO(OH)<sub>2</sub>.
- 5. (4) BF<sub>3</sub>, AlCl<sub>3</sub>, Ag<sup>+</sup>, PCl<sub>3</sub> are Lewis acids.



### General Principles of Extraction of Metals

#### Contents:

- 4.1 Occurrence of Elements
- 4.2 Occurrence of Metals
- 4.3 Metallurgy
- 4.4 Concentration or Dressing of the Ore
- 4.5 Extraction or Isolation of Crude Metals
- **4.6** Thermodynamic Principles of Metallurgy
- **4.7** Applications of Ellingham Diagram in Pyrometallurgy
- **4.8** Third Operation—Refining or Purification
- 4.9 Furnaces
- 4.10 Refractory Materials

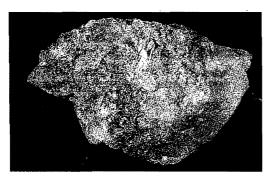


Fig. 4.1 Element in native state:
Gold is so unreactive that it occurs in
the Earth as the metal itself. The vein
of gold are shown in this rock

### 4.1 OCCURRENCE OF ELEMENTS

All materials found in the earth are composed of chemical elements. At present 117\* elements are known but all of them do not occur in nature. Out of the 92 elements from hydrogen to uranium all with the exception of few such as technetium, promethium, astatine, francium, etc., are found in earth. The elements above uranium are man-made which have been synthesised by artificial means. These elements are called **transuranic elements** and are radioactive in nature.

Out of naturally occurring elements, only ten elements make up about 99% mass of the earth's crust, oceans and atmosphere. The first ten most abundant elements in nature (earth's crust, oceans and atmosphere) are:

1. Oxygen	2. Silicon	3. Aluminium	<b>4.</b> Iron	5. Calcium
(49.5%)	(25.7%)	(7.5%)	(4.7%)	(3.4%)
6. Sodium	7. Potassium	8. Magnesium	9. Hydrogen	10. Titanium
(2.6%)	(2.4%)	(1.9%)	(0.87%)	(0.58%)

Thus, a few elements are very abundant, but most of the elements are very scarce. [Some of the common elements such as copper, zinc, tin and lead are not abundant but are found in nature in rich deposits from which these can be easily extracted.]

If the entire universe is considered, then 90% of the matter is hydrogen. Helium is the second most abundant element amounting to 9% and the remaining elements make up only 1% of the universe with oxygen, neon, carbon and nitrogen next in order of decreasing abundance.

The natural mode of occurrence of an element is largely dependent upon its chemical nature. The elements occur in nature sometimes free (or native) but mostly in the combined state.

(i) Native state: The elements which are least reactive and have little or no affinity for oxygen, moisture and other chemical reagents occur in a free or native state, *i.e.*, in uncombined state, *e.g.*, gold (Fig. 4.1), silver and platinum metals are found in native state. Liquid droplets of mercury are

<sup>\*</sup>Recently, elements with atomic numbers 113, 115 and 118 have been reported.

found associated with cinnabar (HgS). Nitrogen, oxygen and noble gases are found in free state in the atmosphere. Carbon in the form of diamond, graphite and coal is found in a free state in earth's crust. Deposits of sulphur are also found deep underground in uncombined state.

(ii) Combined state: Elements which are chemically reactive, *i.e.*, are readily affected by oxygen, moisture, CO<sub>2</sub>, etc., of the atmosphere occur in a combined state in the form of simple or complex compounds. These compounds are called **minerals**. In the combined state, elements are generally present as oxides, carbonates, sulphides, silicates,

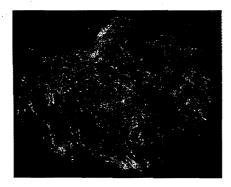


Fig. 4.2 Element in combined state : Ruby, an ore of aluminium, is aluminium oxide,  $Al_2O_3$ , containing a small percentage of chromium oxide,  $Cr_2O_3$ 

halides, sulphates, etc. A few common elements along with their nature of occurrence have been listed in the following table.

### SOME COMMON ELEMENTS WITH THEIR NATURE OF OCCURRENCE

Element	Nature of	Name of	Composition of
Element	occurrence	minerals	minerals
Aluminium	Oxide	Bauxite	Al <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O
		Corundum	$Al_2O_3$
		Diaspore	Al <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O
	Fluoride	Cryolite	Na <sub>3</sub> AlF <sub>6</sub>
	Silicate	China clay	Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> ·2H <sub>2</sub> O
		Mica	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
*		Feldspar	KAlSi <sub>3</sub> O <sub>8</sub>
Calcium	Carbonate	Limestone	CaCO <sub>3</sub>
		or calcite	•
		Dolomite	CaCO <sub>3</sub> ·MgCO <sub>3</sub>
	Fluoride	Fluorspar	CaF <sub>2</sub>
	Sulphate	Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O
Copper	Carbonate	Malachite	CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>
		Azurite	2CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>
	Sulphide	Copper pyrites	CuFeS <sub>2</sub>
	•	Chalcocite or	Cu <sub>2</sub> S
	*	Copper glance	
Iron	Sulphide	Iron pyrites	FeS <sub>2</sub>
	Oxide	Haematite	Fe <sub>2</sub> O <sub>3</sub>
		Magnetite	Fe <sub>3</sub> O <sub>4</sub>
		Limonite	Fe <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O

	Carbonate	Siderite	FeCO <sub>3</sub>
Lead	Carbonate	Cerussite	PbCO <sub>3</sub>
	Sulphate	Anglesite	PbSO <sub>4</sub>
	Sulphide	Galena	PbS
Magnesium	Sulphate	Epsom salt	MgSO <sub>4</sub> ·7H <sub>2</sub> O
	Chloride	Carnallite	KCl·MgCl <sub>2</sub> ·6H <sub>2</sub> O
•	Carbonate	Magnesite	MgCO <sub>3</sub>
Manganese	Oxide	Pyrolusite	MnO <sub>2</sub>
Mercury	Sulphide	Cinnabar	HgS
Silver	Sulphide	Argentite or	Ag <sub>2</sub> S
		Silver glance	
	Chloride	Horn silver	AgCl
Zinc	Sulphide	Zinc blende	ZnS
	Oxide	Zincite	ZnO
	Carbonate	Calamine	ZnCO <sub>3</sub>
Sodium	Carbonate	Trona	Na <sub>2</sub> CO <sub>3</sub> ·2NaHCO <sub>3</sub> ·3H <sub>2</sub> O
		Natron	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
	Sulphate	Glauber's salt	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O
	Chloride	Common salt	NaCl
Potassium	Nitrate	Indian nitre	KNO <sub>3</sub>
	Chloride	Carnallite	KCl-MgCl <sub>2</sub> -6H <sub>2</sub> O
		Sylvine	KC1
Silicon	Oxide	Sand, quartz	SiO <sub>2</sub>
		or flint	-
	Silicates	Constituent of	
		igneous rocks	
		which consists	
		of silicates of	
		Mg, Al, K or Fe	-
Phosphorus	Phosphate	Phosphorite	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>
1 Hospitorus	Thospitate	-	
The anima	Fluoride	Fluorapatite	3Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·CaF <sub>2</sub>
Fluorine	riuoriae	Fluorspar	CaF <sub>2</sub>
n .	D .1	Cryolite	Na <sub>3</sub> AlF <sub>6</sub>
Bromine	Bromide	Bromocarnallite	KBr· MgBr <sub>2</sub> · 6H <sub>2</sub> O
		Sea water contact	
		bromides of Na,	•
Iodine	Indata	K, Mg and Ca	NaIO
юшие	Iodate Iodide	Caliche	NaIO <sub>3</sub>
*	iouide	Kelp-ashes of seaweeds	
		seaweeds contain iodides	+ + + + + + + + + + + + + + + + + + +
		contain louides	

Earth is the storehouse of a large number of elements. The distribution of these elements is not uniform. The elements are distributed in three main parts of the earth known as atmosphere, hydrosphere and lithosphere.

- **(A) Atmosphere :** It is a blanket of gases which is surrounding the lithosphere and hydrosphere parts of the earth. It has no well defined upper limits and gradually merges with the outer space. Of the total mass of atmosphere, about 99% is within a height of 30 km from the earth's surface. The major gases in the atmosphere are nitrogen (78%) and oxygen (21%) by volume. Remaining 1% account for other gases such as argon, neon, krypton, xenon, helium, carbon dioxide, etc.
- **(B) Hydrosphere:** The liquid phase of the earth is called the **hydrosphere**. It covers about 80% of the earth's surface and constitutes lakes, streams, rivers and oceans. There are

a large number of elements in the form of their dissolved salts present in sea water.

Although, sea water contains elements like Na, Mg, Ca, K, Sr, Ba, Cl, Br, S, Li, Al, Rb, etc., only four elements Na, Mg, Cl and Br are commercially obtained from sea water. Sulphur, tin, gold, natural gas and petroleum are also being obtained from sea sources. Iodine, agar-agar, laminarin are the products which are recovered from seaweeds. Efforts are on to extract some of the rare metals from the rock-like objects called **nodules** found on the sea floor.

**(C) Lithosphere:** It is the outermost solid part of the earth and consists of different types of rocks. Almost all the naturally occurring elements are found in the lithosphere. It consists of different types of rocks in which various elements are present in the form of minerals. The distribution of main

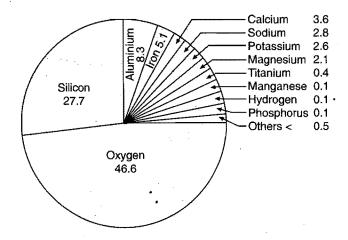


Fig. 4.3 Percentage distribution of different elements in lithosphere

elements in terms of their relative abundance in the lithosphere is shown in Fig. 4.3. It is observed that,

- (i) Oxygen and silicon constitute about 73% by mass of the earth's crust.
- (ii) First five elements comprise almost 92% by mass of the earth's crust.
- (iii) Aluminium is the most abundant normal or representative element.
- (iv) Iron is the most abundant transition metal.
- (v) First ten make up over 99.5% and first twenty make up 99.97% by mass of the earth's crust.

#### Elements in Living Organisms

Animals and plants organisms consist of complex substances composed of both metallic and non-metallic elements. When the analysis of ash of animal tissues is carried out, it is observed that about 30 elements are present in the animal tissues. Abundance of selected elements in the human body (mass %) is given ahead:

O	65.0	Mg	 0.5
C	18.0	K	0.34
H	10.0	S	0.26
N	3.0	Na	0.14
Ca	2.4	Cl	0.15
P	1.0 *	· Fe	0.005

Besides these, the following elements are present in very small amounts:

Cu, Zn, Co, Mn, Mo, I and F.

Many elements get accumulated in living organisms. Some examples are: (i) iodine in seaweeds (ii) vanadium in cucumbers (iii) potassium in plants. The reason for such accumulation is not yet known. Living organisms also contain different elements in different parts. For example:

- (i) Carbon, hydrogen, nitrogen and oxygen are the major constituents of biomolecules which are present in the bodies of animals and plants.
- (ii) Iron is present in haemoglobin—a red pigment of blood cells.
- (iii) **Magnesium** is a constituent of chlorophyll—a green pigment of plants responsible for photosynthesis.
- (iv) Zinc is present in the eyes of certain animals.
- (v) Manganese, iron and copper are present in chloroplasts.
- (vi) Calcium and phosphorus are present in the teeth and bones of animals.

It is important to note that very little is known as to why a particular element is present in a specific region of the living organism. However, it is known that deficiency of a particular element in the living organism brings many disorders. For example, deficiency of iron causes anaemia while that of iodine causes goitre. Similarly, the deficiency of nitrogen, phosphorus and potassium in plants retards their growth.

# 4.2 OCCURRENCE OF METALS (Minerals and Ores)

The earth's crust is the biggest source of metals. Metals occur in nature sometimes free but mostly in a combined state. The rocks in which metals occur in the native state or combined state (in the form of compounds) are called minerals. Every mineral has a definite composition. It may be a single compound or a complex mixture, usually associated with a number of impurities. The minerals from which the metals can be conveniently and economically extracted are known as ores.

All the ores are minerals but all minerals cannot be ores. For example, iron is found in the earth's crust as oxides, sulphides and carbonate.

Haematite	$Fe_2O_3$
Magnetite	$Fe_3O_4$
Iron pyrites	FeS <sub>2</sub>
Copper pyrites	CuFeS <sub>2</sub>
Siderite	FeCO <sub>3</sub>

Out of the above minerals iron is extracted from oxides. Thus, oxides of iron, *i.e.*, **haematite**, **magnetite**, etc., are the **ores of iron**. The minerals of copper are:

Cuprite	Cu <sub>2</sub> O
Copper glance	Cu <sub>2</sub> S
Copper pyrites	CuFeS <sub>2</sub>
Malachite	CuCO <sub>3</sub> · Cu(OH) <sub>2</sub>
Azurite	2CuCO <sub>3</sub> · Cu(OH) <sub>2</sub>

Copper is conveniently and economically extracted from copper pyrites. Thus, **copper pyrites** is the **ore of copper.** Similarly, aluminium has several minerals such as:

Bauxite	$Al_2O_3$ · $2H_2O$
Cryolite	Na <sub>3</sub> AlF <sub>6</sub>
China clay	Al <sub>2</sub> O <sub>3</sub> · 2SiO <sub>2</sub> · 2H <sub>2</sub> O
Feldspar	KAlSi <sub>3</sub> O <sub>8</sub>
Mica	K2O:3Al2O2: 6SiO2: 2H2O

However, the mineral bauxite is used for the extraction of aluminium. Thus, bauxite is an ore of aluminium.

It is evident from the above examples that a metal may occur in a number of minerals but every mineral is not suitable for the extraction of the metal. This is because the mineral may contain low concentration of metal or may contain a large concentration of impurities which may not be easy to remove or process of extraction may not be feasible or commercially viable.

Ores may be divided into four groups:

- (i) **Native ores:** These ores contain metals in a free state, e.g., silver, gold, platinum, mercury, copper, etc. These are found usually associated with rock or alluvial materials like clay, sand, etc. Sometimes lumps of pure metals are also found. These are termed **nuggets**. Iron is found in free state as meteorites which also have 20 to 30% nickel.
- (ii) Sulphurise.1 and arsenical ores: These ores consist of sulphides and arsenides in simple and complex forms of metals. Important ores of this group are:

Metal	Name of the ore	Composition
Pb	Galena	PbS
Zn	Zinc blende	ZnS
Hg	Cinnabar	HgS
Ag	Argentite or silver glance	Ag <sub>2</sub> S
Ni	Kupfer nickel	NiAs
Cu	Copper pyrite	CuFeS <sub>2</sub>

(iii) Halide ores: Metallic halides are very few in nature. Chlorides are most common. For example,

Metal	Name of the ore	Composition
Na	Common salt	NaCl
K and Mg	Carnallite	KCl· MgCl <sub>2</sub> · 6H <sub>2</sub> O
Ag	Horn silver	AgCl

(iv) Oxidised ores: In these ores, metals are present as their oxides or oxysalts such as carbonates, sulphates, phosphates, silicates, etc.

Important ores of this group are:

Metal	Name of the o	ore Composition
Al	Bauxite	Al <sub>2</sub> O <sub>3</sub> · 2H <sub>2</sub> O
·Sn	Tin stone	SnO <sub>2</sub>
	(cassiterite)	
Mn	Pyrolusite	$MnO_2$
Cr	Chromite	FeO Cr <sub>2</sub> O <sub>3</sub>
Zn	Zincite	ZnO
Ti	Ilmenite	FeO· TiO <sub>2</sub>
Fe	Haematite	Fe <sub>2</sub> O <sub>3</sub>
	Magnetite	$Fe_3O_4$
Ca	Limestone	CaCO <sub>3</sub>
Mg	Magnesite	MgCO <sub>3</sub>
Zn	Calamine	$ZnCO_3$
Ba	Barytes	BaSO <sub>4</sub>
Ca	Gypsum 🗻	CaSO <sub>4</sub> 2H <sub>2</sub> O
Li	Lepidolite	(Li,Na,K)2Al2(SO4)3(F,OH)2
	Triphylite	(Li,Na) <sub>3</sub> PO <sub>4</sub> · (Fe,Mn) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>
Be	Beryl	3BeO· Al <sub>2</sub> O <sub>3</sub> · 6SiO <sub>2</sub>



#### **METALLURGY**

The whole process of obtaining a pure metal from one of its ores is known as metallurgy.

In order to extract the metals from ores, several physical and chemical methods are used. The method used in a particular case depends upon the nature of the ore, the properties of the metal and the local conditions. Thus, it is not possible to have a universal method for the extraction of all the metals from their ores. However, the metallurgy of a metal involves three main operations:

- (i) Concentration or dressing of the ore.
- (ii) Isolation of the metal in crude state from the concentrated ore.
- (iii) Purification or refining of the crude metal.

## CONCENTRATION OR DRESSING OF THE ORE

The ores usually are obtained after mining in the form of big lumps. These are broken into small pieces with the help of *crushers* or *grinders*. This process is called **crushing**. These pieces are then converted into a fine powder with the help of either a *ball mill* or *stamp mill*. This process is termed **pulverisation**.

The ores usually contain soil, sand, stones and other useless silicates. These undesired impurities present in ores are called **gangue** (pronounced "gang") or **matrix**. The removal of these impurities from the ores is known as **concentration** or **dressing** or **benefaction** of the ore. To separate the useful minerals from the gangue, both physical and chemical methods are used depending on the ore. It can be done in a number of ways depending upon the nature of the impurities.

#### (A) Gravity Separation

This separation is based on the difference in the specific gravities of the gangue particles and the ore particles. The powdered ore is agitated with water or washed with a running stream of water. The heavy ore particles settle down while the lighter particles of sand, clay, etc., are washed away. For this either Wilfley table or hydraulic classifier is used. Wilfley table is a wooden table having a slanting floor on which long wooden strips called riffles are fixed (Fig. 4.4).

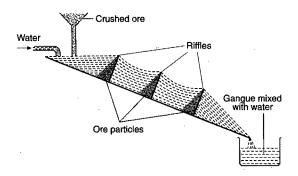


Fig. 4.4 The Wilfley table

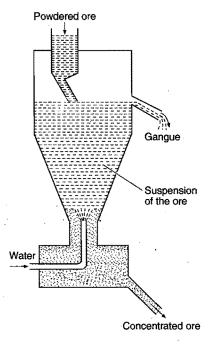


Fig. 4.5 Gravity process

The powdered ore is suspended in a stream of water. The heavier ore particles collect behind the riffles and the gangue particles are carried away with the stream of water. Hydraulic classifier is shown in Fig. 4.5. Powdered ore is dropped from the top of classifier and a strong stream of water is introduced from the bottom. The lighter gangue particles are carried away by the water while the heavier ore particles settle down. Generally, **oxide** and **carbonate ores** are concentrated by this method. For example, tin ore (cassiterite) and iron ore (haematite) are concentrated by gravity method.

#### (B) Electromagnetic Separation

When one component, either the ore or impurity, is magnetic in nature, this method can be used for separation. A magnetic separator consisting a belt moving on two rollers is used, one of which is a strong magnet. The powdered ore is dropped on the belt from one end (non-magnetic) and at the other end (magnetic) the magnetic particles are attracted and fall nearer the roller while non-magnetic particles fall away from the roller. Ferro-magnetic ores are concentrated by this method. For example, wolframite (FeWO<sub>4</sub>)—a magnetic ore, is separated from the non-magnetic ore, cassiterite (SnO<sub>2</sub>) by this method.

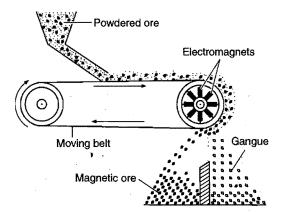


Fig. 4.6 Electromagnetic separation

#### (C) Froth Floatation Process

Froth floatation is a physical method of separating mineral from the gangue that depends on differences in their wettabilities by a liquid solution. This method is used for the concentration of sulphide ores. The method is based on the preferential wetting properties with the frothing agent and water. The powdered ore is added to water containing pine oil (frothing agent) and sodium ethyl xanthate (collecting agent). Cresols and aniline are also added. They act as froth stabilizers. A vigorous stream of air is now passed through, which thoroughly agitates the mixture and disposes the oil into colloid sized particles. As a result of this, the sulphide particles of the ore stick to the oil droplets and rise to the

surface in the form of froth supported by air bubbles. Water wets the gangue particles which sink to the bottom. With this method, it is possible to concentrate the dense ores such as galena and zinc blende.

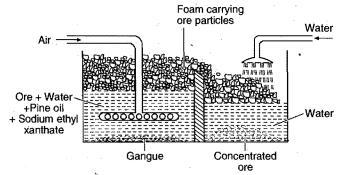


Fig. 4.7 Froth floatation process

Sometimes **depressants** are used to prevent certain type of particles from forming the froth with the bubbles. In the concentration of galena ore, sodium cyanide is added as a depressant for zinc sulphide (ZnS). NaCN forms a layer of zinc complex, Na<sub>2</sub>Zn(CN)<sub>4</sub> on the surface of ZnS and thereby prevents it from the formation of froth while PbS forms a froth. Thus, PbS is separated from ZnS.

#### (D) Leaching

It is a chemical separation. It involves the treatment of the ore with a suitable reagent as to make it soluble while impurities remain insoluble. The insoluble impurities are separated by filteration. The impurities, in this case, include not only gangue but also chemical entities which are not solubilized during leaching operation. The following examples illustrate the procedure.

(i) Leaching of alumina from bauxite ore: Bauxite ore contains ferric oxide, titanium oxide and silica as impurities. When the powdered ore is digested with an aqueous solution (45%) of sodium hydroxide at about 200°C under pressure (35–36 bar), the alumina dissolves forming sodium aluminate while ferric oxide (Fe<sub>2</sub>O<sub>3</sub>), TiO<sub>2</sub> and silica remain as insoluble part.

$$Al_2O_3 \cdot 2H_2O + 2NaOH + H_2O \longrightarrow 2Na[Al(OH)_4]$$
Sodium aluminate (Soluble)

The solution of sodium aluminate is filtered. It may also contain some sodium silicate and free sodium hydroxide. The filtrate is neutralised by passing  $CO_2$  gas, the hydrated  $Al_2O_3$  gets precipitated. At this point, the solution is seeded with freshly precipitated aluminium hydroxide which induces the precipitation.

$$2Na[Al(OH)_4] + 2CO_2 \longrightarrow Al_2O_3 \cdot xH_2O + 2NaHCO_3$$

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to about 1200°C to get pure alumina.

$$Al_2O_3$$
  $xH_2O \xrightarrow{1200$ °C  $Al_2O_3 + xH_2O$ 

[The above process is known as Baeyer's process.]

(ii) Leaching of silver and gold: Gold and silver are extracted from their native ores or silver from argentite ore  $(Ag_2S)$  by leaching. This is also known as Mac-Arthur Forest cyanide process.

In this process, the finely powdered argentite ore or the native silver particles, or the native gold particles are treated with a dilute solution (0.5%) of sodium or potassium cyanide while a current of air is continuously circulated. As a result silver and gold dissolve by forming respective complex cyanides. The impurities remain unaffected. These are filtered off.

$$4Ag + 8NaCN + O_2 + 2H_2O \longrightarrow 2Na[Ag(CN)_2] + 4NaOH$$
 Sodium dicyanoargentate (I) (Soluble) 
$$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$$
 
$$Na_2S \text{ is largely oxidised to } Na_2SO_4.$$
 
$$4Na_2S + 2H_2O + 5O_2 \longrightarrow 2Na_2SO_4 + 2NaOH + 2S$$
 
$$4Au + 8NaCN + O_2 + 2H_2O \longrightarrow 2Na[Au(CN)_2] + 4NaOH$$
 Sodium dicyanoaurate (I) (Soluble)

Ag or Au is recovered from the solution by the addition of electropositive metal like zinc.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

$$2Na[Au(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Au$$
Sodium tetracyanozincate (II)
(Soluble)

## EXTRACTION OR ISOLATION OF CRUDE METALS (Oxidation/Reduction)

Metals are usually extracted by reduction. Thus, the concentrated ore is converted into a form which is suitable for reduction. Oxides are easier to reduce, therefore, the extraction of metals involves the following two major steps:

- (1) Conversion of the ore into metallic oxide
- (2) Reduction of the metallic oxide to the free metal.

#### Conversion of the ore into metallic oxide

The ores of the metals are usually in the form of hydrated oxides, carbonates, sulphides, etc. Depending upon the nature of the ores, two methods are used for conversion into oxides.

**Note:** The ores which are already in anhydrous form—for example, rutile (TiO<sub>2</sub>)—are not subjected to these methods. After concentration, these are directly reduced.

(A) Calcination: This method is commonly used to convert hydrated oxides or hydroxides and carbonates into respective oxides. It involves heating of the ore below its

**fusion temperature in absence of air.** This step is generally performed in a **reverberatory furnace**. The concentrated ore is put on the hearth of the furnace and heated by flames deflected from the roof. During calcination the following changes may occur.

Moisture is driven out. Water is removed from hydrated oxides or hydroxides. Organic matter is expelled.

$$\begin{array}{ccc} \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} & \xrightarrow{\text{Heat}} & \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O} \\ \text{Bauxite} & & \text{Alumina} \\ \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} & \xrightarrow{\text{Heat}} & \text{Fe}_2\text{O}_3 & + 3\text{H}_2\text{O} \\ \text{Limonite} & & \text{Ferric oxide} \end{array}$$

Carbonates lose carbon dioxide and are converted into corresponding oxides.

$$\begin{array}{c} \text{CaCO}_3 & \xrightarrow{\text{Heat}} & \text{CaO} & + \text{CO}_2 \\ \text{Calcium oxide} & \xrightarrow{\text{Calcium oxide}} & \\ \text{CaCO}_3 \cdot \text{MgCO}_3 & \xrightarrow{\text{Heat}} & \text{CaO} + \text{MgO} & + \text{CO}_2 \\ \text{Dolomite} & & \text{Magnesium oxide} \\ \text{CuCO}_3 \cdot \text{Cu(OH)}_2 & \xrightarrow{\text{Heat}} & \text{2CuO} + \text{H}_2\text{O} + \text{CO}_2 \\ \text{Malachite} & & \text{Cupric oxide} \\ & & \text{ZnCO}_3 & \xrightarrow{\text{Heat}} & \text{ZnO} & + \text{CO}_2 \\ \text{Calamine} & & \text{Zinc oxide} \\ \end{array}$$

The material becomes porous which can be easily reduced in the subsequent step.

- **(B) Roasting:** It is a process in which the ore is heated in presence of air. During this operation, the temperature is kept below the melting point of the ore. The sulphide ores are generally subjected to roasting. The roasting is generally done in a reverberatory furnace or in a small blast furnace. As a result of roasting, the following changes occur.
  - (i) Moisture is driven out.
  - (ii) Organic matter is burnt.
- (iii) The non-metallic impurities such as sulphur, phosphorus, arsenic are converted into respective volatile oxides which get removed.

$$S_8 + 8O_2 \longrightarrow 8SO_2$$
 (Sulphur dioxide)  
 $P_4 + 5O_2 \longrightarrow P_4O_{10}$  (Phosphorus pentoxide)  
 $4As + 3O_2 \longrightarrow 2As_2O_3$  (Arsenious oxide)

Sulphide ores are converted into metallic oxides.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$Lead oxide$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$Cuprous oxide$$

The sulphur dioxide thus evolved is utilised for the manufacture of  $H_2SO_4$ .

In the extraction of copper, the ore is copper pyrites (CuFeS<sub>2</sub>) which consists of FeS also. The ore is mixed with silica before roasting. During heating, initially a mixture of Cu<sub>2</sub>S and FeS is formed.

$$2CuFeS_2 \longrightarrow Cu_2S + 2FeS + S$$
$$S + O_2 \longrightarrow SO_2$$

Most of the FeS is converted into FeO which combines with silica to form iron silicate (FeSiO<sub>3</sub>)—a **slag** (fusible in nature).

Copper is obtained in the form of copper matte which contains Cu<sub>2</sub>S and small amount of FeS.

The material becomes porous which can be made easily workable in the subsequent step.

In some cases chlorinating roasting is done as metal is obtained by reduction of halide (usually chloride). For example, silver ores are heated with sodium chloride.

$$Ag_2S + 2NaCl \longrightarrow AgCl + Na_2S$$

**Note:** (i) Calcination and roasting may be carried out in the same reverberatory furnace. During calcination, air holes are partially or completely closed while in roasting, the air holes are open.

(ii) When roasting is done at moderate temperature, the sulphide ore is partially oxidised into oxide and partially into sulphate. For example, in the roasting of galena and zinc blende.

$$\begin{array}{l} \text{2PbS} + 3\text{O}_2 \longrightarrow \text{2PbO} + 2\text{SO}_2 \\ \text{PbS} + 2\text{O}_2 \longrightarrow \text{PbSO}_4 \\ \text{2ZnS} + 3\text{O}_2 \longrightarrow \text{2ZnO} + 2\text{SO}_2 \\ \text{ZnS} + 2\text{O}_2 \longrightarrow \text{ZnSO}_4 \end{array}$$

### 2. Reduction of the metallic oxide to the free metal

The crude metal is obtained when the roasted or calcined ore is put to reduction by using a suitable reducing agent. The selection of a suitable reducing agent depends upon the reactivity of the metal. Some of the methods commonly used to get the free metal from the roasted or calcined ore are briefly described here.

#### (A) Smelting

This involves reduction of ore to the molten metal at a high temperature. For the extraction of less electropositive metals such as Pb, Zn, Fe, Sn, etc., powerful reducing agents such as C, H<sub>2</sub>, CO, water gas, Na, K, Mg, Al may be used. Some examples are given below:

$$PbO + C \longrightarrow Pb + CO$$

$$WO_3 + 3H_2 \longrightarrow W + 3H_2O$$

$$CuO + CO \longrightarrow Cu + CO_2$$

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$

The process of extracting the metal by heating the metal oxide with a suitable reducing agent is called pyrometallurgy.

Out of the various reducing agents, carbon, carbon monoxide and aluminium are generally used.

**(i) Carbon reduction process:** It is generally called **smelting.** The oxides of less electropositive metals are reduced by strongly heating them with coal or coke. Carbon combines with the oxygen of the metal oxide to form carbon monoxide which can also act as a reducing agent.

$$M_x O_y + y C \longrightarrow x M + y CO$$

$$PbO + C \longrightarrow Pb + CO$$

$$PbO + CO \longrightarrow Pb + CO_2$$
Similarly,
$$Fe_2 O_3 + 3C \longrightarrow 2Fe + 3CO$$

$$Fe_2 O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

The ores, even after concentration, contain some gangue. To remove gangue, certain substances are mixed with concentrated ore which combine with the gangue to form a fusible material which is not soluble in molten metal. The substances used are called **fluxes** and the fusible material formed during reduction process is called **slag**. Slag is usually lighter and floats on the surface of the molten metal.

Fluxes are classified as (i) Acidic flux and (ii) Basic flux. An acidic flux (e.g., silica, borax, etc.,) is the chemical substance which removes the basic impurities.

$$SiO_2$$
 +  $CaO$   $\longrightarrow$   $CaSiO_3$   
Acidic flux Basic impurity Slag  
(Gangue)

The basic flux (e.g., limestone, magnesite, ferric oxide, etc.,) is the chemical substance which removes the acidic impurities.

$$MgCO_3$$
 +  $SiO_2$   $\longrightarrow$   $MgSiO_3$  +  $CO_2$   
Basic flux Acidic impurity  $Slag$  (Gangue)

(ii) Reduction by aluminium (Goldschmidt aluminothermic process): This process is employed in the case of those metals which have very high melting points and are to be extracted from their oxides. Their reduction with carbon

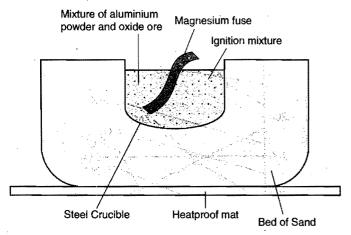


Fig. 4.8 An apparatus for thermite reaction

is not satisfactory. A mixture of concentrated oxide ore and aluminium powder, commonly called as **thermite**, is taken in a steel crucible placed in a bed of sand. The reaction is started by the use of an ignition mixture containing magnesium powder and barium peroxide.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$

$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$$

Large amount of heat energy is released during reduction, which fuses both the alumina and the metal.

#### (B) Self Reduction Process

This process is also called autoreduction process or air reduction process. The sulphide ores of less electropositive metals like Hg, Pb, Cu, etc., are heated in air as to convert part of the ore into oxide or sulphate which then reacts with the remaining sulphide ore to give the metal and sulphur dioxide. No external reducing agent is used in this process.

$$\begin{array}{c} 2 HgS + 3 O_2 \longrightarrow 2 HgO + 2 SO_2 \\ 2 HgO + HgS \longrightarrow 3 Hg + SO_2 \end{array} \end{array} \begin{array}{c} \text{Extraction of Hg} \\ \text{from cinnabar ore} \end{array}$$
 
$$\begin{array}{c} 2 Cu_2S + 3O_2 \longrightarrow 2 Cu_2O + 2 SO_2 \\ Cu_2S + 2 Cu_2O \longrightarrow 6 Cu + SO_2 \end{array} \end{array} \begin{array}{c} \text{Extraction of Cu} \\ \text{from copper glance} \end{array}$$
 
$$\begin{array}{c} 2 PbS + 3O_2 \longrightarrow 2 PbO + 2 SO_2 \\ 2 PbO + PbS \longrightarrow 3 Pb + SO_2 \end{array} \end{array} \begin{array}{c} \text{Extraction of lead} \\ \text{from galena ore} \end{array}$$

#### (C) Electrolytic Reduction

The oxides of the highly electropositive metals like Na, K, Mg, Ca, Al, etc., cannot be reduced easily with carbon at moderate temperatures. For reduction, a very high temperature is required at which the metal may combine with carbon to form a carbide. These metals are thus extracted by the electrolysis of their oxides, hydroxides or chlorides in fused state. Sometimes, a small amount of some other salt is

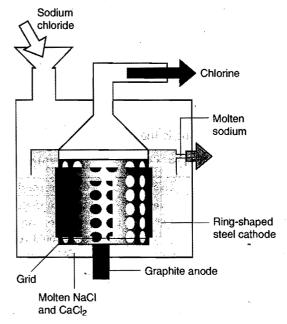


Fig. 4.9 Production of sodium metal from fused mixture of NaCl and CaCl<sub>2</sub> by Electrolytic reduction by the Down's process

added to lower the fusion temperature or to increase the conductivity or both. The metal is liberated at the cathode. Sodium is obtained by the electrolysis of fused mixture of NaCl and CaCl<sub>2</sub> (**Down's process**) or by electrolysis of fused sodium hydroxide (**Castner's process**).

NaCl
$$\uparrow | Fused$$
Cathode  $\longleftarrow$  Na<sup>+</sup> + Cl<sup>-</sup>  $\longrightarrow$  Anode
$$Na^{+} + e \longrightarrow Na \qquad Cl^{-} - e = Cl$$

$$2Cl \longrightarrow Cl_{2}$$

Aluminium is obtained by the electrolysis of alumina mixed with cryolite.



### THERMODYNAMIC PRINCIPLES OF METALLURGY

The basic concepts of thermodynamics are quite helpful in selecting which element will be the most suitable reducing agent for a particular oxide during a metallurgical operation. It can also predict the optimum temperature at which the reduction can occur smoothly.

For any reaction or process, Gibb's Helmholtz free energy change ( $\Delta G$ ) is given by the equation,

$$\Delta G = \Delta H - T \Delta S \qquad \dots (i)$$

where  $\Delta H$  is the enthalpy change and  $\Delta S$  is the entropy change and T is the absolute temperature at which the reaction is carried out. For the feasibility of any reaction at any temperature the value of  $\Delta G$  must be negative at that temperature. The free energy change is also related to the equilibrium constant 'K' of the reaction at temperature T by the following equation,

$$\Delta G = -RT \ln K$$
 ... (ii)

A negative  $\Delta G$  implies a +ve K in the above equation. This can happen only if the reaction proceeds towards the products. The following conclusions can be drawn:

(i) Greater the negative value of free energy change ( $\Delta G$ ), more spontaneous is the reaction.

#### CONDITIONS FOR $\Delta G$ TO BE NEGATIVE

ΔΗ	ΤΔS	Favourable conditions
- ve (Exothermic)	+ ve	Any temperature
<ul><li>ve (Exothermic)</li></ul>	– ve	$\Delta H > T \Delta S$
		(Temp. should be low)
+ ve (Endothermic)	+ ve	$T\Delta S > \Delta H$
		(Temp. should be high)

(ii) If two reactions are put together in a system and the net  $\Delta G$  of both the reactions is –ve, the overall reaction will occur, *i.e.*, a reaction with  $\Delta G$  positive can be made to occur if it is coupled with another reaction having a large negative  $\Delta G$  so that the net  $\Delta G$  of both the reactions is negative.

Such coupling reactions can be easily understood through **Ellingham diagram.** 

#### **Ellingham Diagram**

Ellingham diagram consists of graphs which represent the variation of standard free energy with temperature of the formation of oxides of various elements, *i.e.*, plots of  $\Delta_f G^\circ vs$  T. Similar plots can also be plotted for sulphides and halides. These were first plotted by H.J.T. Ellingham. These diagrams help us in predicting the feasibility of thermal reduction of an ore.

Consider the formation of a metal oxide  $(M_xO)$ .

$$2xM(s) + O_2(g) \longrightarrow 2M_xO(s)$$

In this reaction, there is decrease in the value of  $\Delta S^{\circ}$  as  $M_xO$  is solid and  $O_2$  is a gas, *i.e.*,  $\Delta S$  is negative. Thus, if temperature is increased,  $T\Delta S^{\circ}$  becomes more negative.

As in the equation,

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

 $T\Delta S^{\circ}$  is subtracted, therefore,  $\Delta G^{\circ}$  becomes less negative, *i.e.*,  $\Delta G^{\circ}$  is likely to increase with rise in temperature and this trend is confirmed from the curves of metal oxides in Fig. 4.10. The following observations are made from the curves.

- (i) The slope of the curves of the formation of metal oxides is +ve because  $\Delta G^{\circ}$  becomes less negative or increases with the rise in temperature.
- (ii) Each curve is a straight line except when some change takes place in phase  $(s \longrightarrow l \text{ or } l \longrightarrow g)$ . The temperature at which such a change occurs is indicated by an increase in the slope on the +ve side. For example, in the Zn—ZnO curve, the melting of zinc is indicated by an abrupt increase in the +ve slope at temperature 692 K.

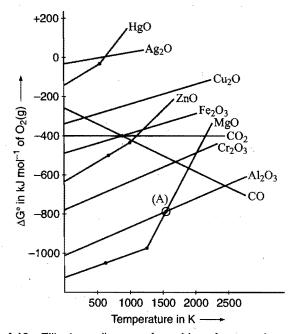


Fig. 4.10 Ellingham diagrams for oxides of some elements

(iii) In the case of less reactive metals like silver and mercury,  $\Delta G^{\circ}$  becomes positive at high temperatures. It indicates that both silver oxide (Ag<sub>2</sub>O) and mercury oxide (HgO) are unstable and decompose at high temperature.

$$2Ag_2O \xrightarrow{\text{Heat}} 4Ag + O_2$$

$$2HgO \xrightarrow{\text{Heat}} 2Hg + O_2$$

- (iv) In the curve of CO,  $\Delta G^{\circ}$  decreases as  $\Delta S^{\circ}$  increases. This is indicated by the downward trend.
- (v) Any metal oxide with lower value of  $\Delta G^{\circ}$  is more stable than a metal oxide with higher  $\Delta G^{\circ}$ . This implies that the metal oxide placed higher in the diagram can be reduced by the metal involved in the formation of the oxide placed lower in the diagram. For example,  $\operatorname{Cr_2O_3}$  can be reduced by Al metal but  $\operatorname{Al_2O_3}$  cannot be reduced by Cr.

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$

Thus, the relative tendency of the various metals to act as reducing agents is:

#### Limitations of Ellingham Diagram

Ellingham diagram simply tells whether the reduction of a particular oxide with a specific reducing agent is possible or not. However, it does not tell anything about the kinetics of the reduction process, *i.e.*, whether the reduction is fast or slow.

The interpretation of  $\Delta G^{\circ}$  is based on the equilibrium constant, 'K'.

$$\Delta G^{\circ} = -RT \ln K$$

Thus, it is presumed that the reactants and products are in equilibrium:

$$M_rO + A \Longrightarrow xM + AO$$

But, this is not always true because the reactant/product may be solid.

#### Reducing Nature of Carbon

Carbon in the form of coke, charcoal or carbon monoxide is used as a reducing agent in pyrometallurgical operations. Such a reduction process used in the extraction of a metal is termed **smelting**.

When carbon is to act as a reducing agent, the following three reactions are possible:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$
 ... (i)

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$
 ... (ii)

$$2CO(s) + O_2(g) \longrightarrow 2CO_2(g)$$
 ... (iii)

In the first reaction (formation of CO<sub>2</sub>) there is hardly any change in entropy, *i.e.*,  $\Delta S^{\circ} \approx 0$  and therefore,  $\Delta G^{\circ}$  remains

nearly the same with rise in temperature, i.e.,  $\Delta G^{\circ}$  is independent of temperature.

In the second reaction (formation of CO), there is increase in entropy ( $\Delta S^{\circ}$  is positive) and therefore,  $\Delta G^{\circ}$  becomes more negative with increase in temperature.

However, in third reaction, there is decrease in entropy ( $\Delta S^{\circ}$  is negative) and therefore,  $\Delta G^{\circ}$  becomes less negative with increase in temperature.

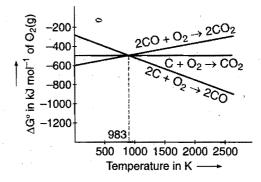


Fig. 4.11 Ellingham diagram for the reducing nature of carbon

The above observations can be seen in Fig. 4.11. The three curves have been found to intersect at 983 K. It implies that above this temperature, the reaction (ii) is most suitable. It means that carbon can reduce any metal oxide at very high temperatures and is then itself oxidised to CO. However, the reduction with carbon at high temperatures is not preferred in all cases due to the following reasons:

- (a) It involves high cost.
- (b) Some metals react with carbon at high temperatures and form carbides.
- (c) There are many practical difficulties in the maintenance of high temperature.

From the plot for the reaction of carbon monoxide with oxygen, it is evident that carbon monoxide acts as a better reducing agent than carbon at temperatures below 983 K.

#### Theory of Reduction of Metal Oxide with Carbon

During reduction the metal oxide decomposes,

$$M_xO(s) \longrightarrow xM(s \text{ or } l) + 1/2 O_2(g)$$
 ... (i)

and the carbon (reducing agent) takes away the oxygen, *i.e.*, it undergoes **oxidation**.

$$C(s) + 1/2 O_2(g) \longrightarrow CO(g)$$
 ... (ii)  
 $\Delta G^{\circ}(C, CO)$ 

or 
$$1/2 C(s) + 1/2 O_2(g) \longrightarrow 1/2 CO_2(g)$$
 ... (iii)  
 $1/2 \Delta G^{\circ}(C, CO_2)$ 

or 
$$CO(g) + 1/2 O_2(g) \longrightarrow CO_2(g)$$
 ... (iv)

$$\Delta G^{\circ}(C, CO_2)$$
 he role of the reducing agent is to provide a large

The role of the reducing agent is to provide a large negative  $\Delta G^{\circ}$  to make the sum of the  $\Delta_r G^{\circ}$  of the above

two reactions, (i.e., reduction of metal oxide and oxidation of carbon or carbon monoxide) negative.

Reversing the equation (i)

$$xM(s \text{ or } l) + 1/2 O_2(g) \longrightarrow M_xO(s)$$
 ... (v)  
 $\Delta G^{\circ}(M, M_xO)$ 

Subtracting equation (v) from equations (ii), (iii) and (iv) respectively, we have,

$$M_xO(s) + C(s) \longrightarrow xM(s \text{ or } l) + CO(g)$$
 ... (vi)  
 $M_xO(s) + 1/2 C(s) \longrightarrow xM(s \text{ or } l) + 1/2CO_2(g)$  ... (vii)  
 $M_xO(s) + CO(s) \longrightarrow xM(s \text{ or } l) + CO_2(g)$  ... (viii)

The equations (vi), (vii) and (viii) describe the reduction of the metal oxide,  $M_x$ O. The  $\Delta_r$ G° values of these equations can be obtained from Ellingham diagram (Fig. 4.10). If  $\Delta_r$ G° values are negative, the reduction is feasible otherwise not. Greater the difference, easier is the reduction.

Without making any calculations for  $\Delta_r G^\circ$ , the prediction about the feasibility of a reduction process can be made by looking at the Ellingham diagram. Metal oxide placed higher in the diagram can be reduced by the element (metal) involved in the formation of the oxide placed lower in the diagram.

It is important to note that if a particular reduction process does not take place at a lower temperature, it may take place at a higher temperature. Ellingham diagram also helps in selecting such a temperature. The temperature is indicated by the intersection of the two curves. For example, the temperature at the intersection point 'A' in Fig 4.10 of two curves for Al  $\longrightarrow$  Al<sub>2</sub>O<sub>3</sub> and Mg  $\longrightarrow$  MgO is approximately 1665 K. Below this temperature Mg reduces Al<sub>2</sub>O<sub>3</sub> into Al but above 1665 K, Al can reduce MgO into Mg.

# 4.7 APPLICATIONS OF ELLINGHAM DIAGRAM IN PYROMETALLURGY

The utility of Ellingham diagram in pyrometallurgy can be illustrated by discussing the extraction of iron, copper and zinc from their respective oxides.

#### (A) Theory of reduction of Haematite

In the Ellingham diagram (Fig. 4.12), there are three curves which illustrate the formation of ferric oxide from iron,

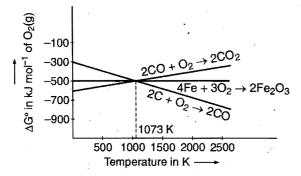


Fig. 4.12 Ellingham diagram for the reduction of haematite

formation of CO from carbon and formation of  $CO_2$  from CO. The curves cross each other at 1073 K.

Above 1073 K,  $\Delta G^{\circ}$  for the formation of Fe<sub>2</sub>O<sub>3</sub> is less negative than  $\Delta G^{\circ}$  for the formation of carbon monoxide from carbon. Thus, above 1073 K, carbon (coke) can reduce Fe<sub>2</sub>O<sub>3</sub>, *i.e.*,  $\Delta_r G^{\circ}$  for the reaction,

$$Fe_2O_3(s) + 3C(s) \xrightarrow{> 1073 \text{ K}} 2Fe(s) + 3CO(g)$$
 is negative.

Below 1073 K,  $\Delta G^{\circ}$  for formation of CO from carbon is less negative than  $\Delta G^{\circ}$  for the formation of Fe<sub>2</sub>O<sub>3</sub>.  $\Delta_r G^{\circ}$  for the reduction of Fe<sub>2</sub>O<sub>3</sub> with carbon will be positive and hence, reduction is not possible. However, it is observed from the diagram that  $\Delta G^{\circ}$  of formation of CO<sub>2</sub> from CO is more negative than  $\Delta G^{\circ}$  of formation of Fe<sub>2</sub>O<sub>3</sub>. This means that Fe<sub>2</sub>O<sub>3</sub> can be reduced by CO below 1073 K, *i.e.*,  $\Delta_r G^{\circ}$  for the reaction,

Fe<sub>2</sub>O<sub>3</sub>(s) + 3CO(s) 
$$\xrightarrow{> 1073 \text{ K}}$$
 2Fe(s) + 3CO<sub>2</sub>(g) is negative.

Thus, in the blast furnace, reduction of  $Fe_2O_3$  occurs in different temperature ranges either below 1073 K by carbon monoxide or above 1073 K by carbon (coke).

#### (B) Theory of reduction of Cu<sub>2</sub>O

#### (i.e., Extraction of copper from cuprous oxide)

In the Ellingham diagram (Fig. 4.13), it is observed that  $Cu_2O$  curve lies almost at the top while the lines showing the formation of  $CO_2$  from C and CO and the formation of CO from carbon lie much below it. So it is quite easy to reduce  $Cu_2O$  to the metal by heating with coke at temperatures after 500–600 K.

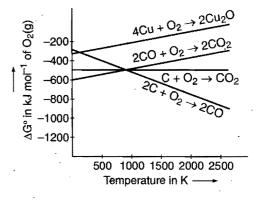


Fig. 4.13 Ellingham diagram for copper and carbon oxides

However, most of the ores of copper are sulphides and contain iron sulphide also. Thus, the ores are first roasted in such a way so that iron is removed and copper sulphide is converted into cuprous oxide.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

The oxide can then be easily reduced to metallic copper by using coke.

$$Cu_2O + C \longrightarrow 2Cu + CO$$

However, this method is not used in actual practice for the extraction of copper.

#### (C) Theory of reduction of ZnO

Ellingham diagram (Fig. 4.14) reveals that the curves involving the formation of ZnO and carbon monoxide cross each other at about  $1270~\rm{K}$ .

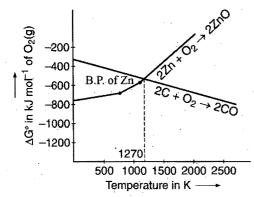


Fig. 4.14 Ellingham diagram for formation of ZnO and CO

There is a sudden increase in the value of  $\Delta G^{\circ}$  for the formation of ZnO above 1180 K. This is due to the fact that zinc begins to boil at this temperature. Above 1270 K,  $\Delta_r G^{\circ}$  of the following equation,

 $ZnO(s) + C(s) \xrightarrow{> 1270 \text{ K}} Zn(g) + CO(g)$  is considerable negative and thus, reduction of ZnO with coke occurs easily.

## 4.8 THIRD OPERATION—REFINING OR PURIFICATION

The metals obtained by the application of above reduction methods from the concentrated ores are usually impure. These impure metals may be associated with small amounts of (a) unchanged ore, (b) other metals produced by the simultaneous reduction of their compounds originally present in the ore, (c) non-metals like silicon, carbon, phosphorus, etc., (d) residual slag, flux, etc. The impure metal is thus subjected to some purifying processes known as refining in order to remove the undesired impurities. The following refining processes may be applied depending upon the nature of the metal under treatment and the nature of the impurities.

- (a) Liquation process: This process is based on the difference in fusibility of the metal and impurities. When the impurities are less fusible than the metal itself, this process is employed. The impure metal is placed on the sloping hearth of a furnace and gently heated. The metal melts and flows down leaving behind the impurities on the hearth. This method is used to purify the metals like Bi, Sn, Pb, Hg, etc.
- **(b) Distillation:** This process is used for those metals which are easily volatile. The impure metal is heated in a retort and its vapours are separately condensed in a receiver.

The non-volatile impurities are left-behind in the retort. This is used for the purification of Zn, Cd, Hg, etc.

- **(c) Pyrometallurgical oxidation process:** This process is used when the impurities have a greater affinity for oxygen than the metal itself. This method is usually employed for refining the metals like Fe, Cu, Ag, etc. The oxidation is done by various ways.
- (i) Cupellation: The impure metal is heated in a cupel or oval shaped crucible made of bone ash or cement and a blast of air is passed over the molten mass. The impurities get oxidised and removed with the blast of air. For example the impurity of lead present in silver is removed by cupellation process.
- (ii) Bessemerisation: The impure metal is heated in a furnace and a blast of compressed air is blown through the molten mass. The impurities get oxidised. For example, the molten pig iron is taken in a bessemer converter and compressed air is passed which oxidises the impurities.

$$\begin{array}{c} 2Mn + O_2 & \longrightarrow 2MnO \\ Si + O_2 & \longrightarrow SiO_2 \\ 2C + O_2 & \longrightarrow 2CO \\ MnO + SiO_2 & \longrightarrow MnSiO_3 \\ Slag \end{array}$$

- (iii) Poling: The impure metal containing oxides as impurity can be purified by this method. The molten impure metal is stirred with green poles of wood. The green poles of wood release the hydrocarbon gases which reduce the oxide impurities. This method is especially used in the purification of copper (old method).
- (d) Electrolytic refining of metals: Many of the metals such as copper, silver, gold, aluminium, lead, etc., are purified by this method. This is perhaps the most important method. The impure metal is made anode while a thin sheet of pure metal acts as a cathode. The electrolytic solution consists of generally an aqueous solution of a salt or a complex of the metal. On passing the current, the pure metal is deposited on the cathode and equivalent amount of the metal gets dissolved from the anode. Thus, the metal is transferred from anode to cathode through solution. The soluble impurities pass into the solution while the insoluble one, especially less electropositive impurities collect below the anode as anodic mud or anode sludge. Some examples are given below:

#### (i) Purification of copper

Impure metal—Anode;

Thin sheets of copper Cathode.

Electrolyte—An aqueous solution of copper sulphate containing H<sub>2</sub>SO<sub>4</sub>.

A current of 1.3 volt is used. Anodic mud contains Ag, Au, Pt, Pd, etc., and impurities like Fe, Zn, Ni, etc., pass into the solution. 99.9% pure copper is obtained.

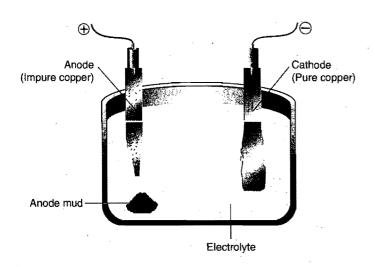


Fig. 4.15 Purification of copper by electrolysis

#### (ii) Purification of silver

Impure metal—Anode; A thin sheet of pure silver—Cathode. Electrolyte—An aqueous solution of AgNO<sub>3</sub> containing HNO<sub>3</sub>.

#### (iii) Purification of lead

Impure metal—Anode; A sheet of pure lead—Cathode. Electrolyte—A solution of lead silico fluoride PbSiF<sub>6</sub> containing 8–10% of H<sub>2</sub>SiF<sub>6</sub>.

- **(e) Special methods:** Sometime some special methods are used for refining or purification of metals, some of which are given below:
- (i) Mond's process: Nickel is purified by this method. Impure nickel is treated with carbon monoxide at 60–80°C when volatile compound, nickel carbonyl, is formed. Nickel carbonyl decomposes at 180°C to form pure nickel and carbon monoxide which can again be used.

Impure nickel + CO 
$$\xrightarrow{60-80^{\circ}\text{C}}$$
 Ni(CO)<sub>4</sub>  $\xrightarrow{180^{\circ}\text{C}}$  Ni + 4CO Gaseous compound

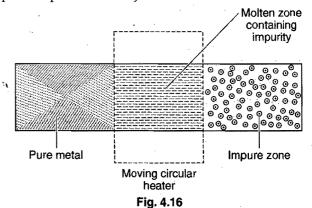
(ii) Van Arkel process: This method is generally applied for obtaining ultrapure metals. The impure metal is converted into a volatile compound while the impurities are not affected. The volatile compound is then decomposed electrically to get the pure metal.

Ti, Zr, Hf, Si, etc., have been refined by this method.

Impure metal + 
$$I_2$$
  $\longrightarrow$  Metal iodide  $\xrightarrow{\text{Tungsten}}$   $\xrightarrow{\text{filament}}$  Metal +  $I_2$   $\xrightarrow{\text{(Pure)}}$   $\xrightarrow{\text{Ti}(s)}$  +  $2I_2(g)$   $\xrightarrow{523 \text{ K}}$   $\xrightarrow{\text{Ti}I_4(g)}$   $\xrightarrow{\text{Impure}}$  Ti $I_4(g)$   $\xrightarrow{\text{Ti}I_4(g)}$   $\xrightarrow{\text{Ti}I_4(g)}$ 

This method is quite expensive.

(iii) Zone refining or Fractional crystallisation: Elements such as Si, Ge, Ga, etc., which are used as semiconductors are refined by this method. Highly pure metals are obtained. The method is based on the difference in solubility of impurities in molten and solid state of the metal. A movable heater is fitted around a rod of the impure metal. The heater is slowly moved across the rod. The metal melts at the point of heating and as the heater moves on from one end of the rod to the other end, the pure metal crystallises while the impurities pass on the adjacent melted zone.



Different metallurgical processes can be broadly divided into three main types.

- **1. Pyrometallurgy:** Extraction is done using heat energy. The metals like Cu, Fe, Zn, Pb, Sn, Ni, Cr, Hg, etc., which are found in nature in the form of oxides, carbonates, sulphides are extracted by this process.
- **2. Hydrometallurgy**: Extraction of metals involving aqueous solution is known as hydrometallurgy. Silver, gold, etc., are extracted by this process.
- **3. Electrometallurgy**: Extraction of highly reactive metals such as Na, K, Ca, Mg, Al, etc., by carrying electrolysis of one of the suitable compound in fused or molten state.

#### **SUMMARY OF THE EXTRACTION OF METALS**

Metal	Main Occurrence	Main Method of Extraction
Sodium	Common Salt, NaCl	Electrolysis of fused NaCl with CaCl <sub>2</sub>
Magnesium	Carnallite, KCl·MgCl <sub>2</sub> ·6H <sub>2</sub> O; Magnesite, MgCO <sub>3</sub>	Electrolysis of fused MgCl2 with KCl
Calcium	Limestone, CaCO <sub>3</sub> ; Gypsum, CaSO <sub>4</sub> ·2H <sub>2</sub> O	Electrolysis of fused CaCl2 and CaF2
Aluminium	Bauxite, Al <sub>2</sub> O <sub>3</sub> 2H <sub>2</sub> O	Electrolysis of Al <sub>2</sub> O <sub>3</sub> in molten Na <sub>3</sub> AlF <sub>6</sub> (cryolite)
Copper	Copper pyrites, CuFeS <sub>2</sub>	Partial oxidation of sulphide ore
	Cuprite, Cu <sub>2</sub> O	$(2Cu2O + Cu2S \longrightarrow 6Cu + SO2)$
Silver	Argentite, Ag <sub>2</sub> S	Hydrometallurgy
	Native silver	$Ag_2S + 4NaCN \longrightarrow 2NaAg(CN)_2 + Na_2S$
		$2NaAg(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2Ag$
Zinc	Zinc blende, ZnS	Reduction of ZnO with carbon or electrolysis of ZnSO <sub>4</sub>
	Calamine, ZnCO <sub>3</sub>	$ZnO + C \longrightarrow Zn + CO$
Lead	Galena, PbS	Reduction of PbO with carbon
		$PbO + C \longrightarrow Pb + CO$
Tin .	Cassiterite, SnO <sub>2</sub>	Reduction of SnO <sub>2</sub> with carbon
		$SnO_2 + 2C \longrightarrow Sn + 2CC$
Iron	Haematite, Fe <sub>2</sub> O <sub>3</sub>	Reduction of oxide with carbon monoxide
	Magnetite, Fe <sub>3</sub> O <sub>4</sub>	$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$
Chromium	Chromite, FeO Cr <sub>2</sub> O <sub>3</sub>	Reduction of Cr <sub>2</sub> O <sub>3</sub> with Al
		$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$
Nickel	Millerite, NiS	Reduction of NiO with CO
		$NiO + 5CO \longrightarrow Ni(CO)_4 + CO_2; Ni(CO)_4 \longrightarrow Ni + 4CO$
Mercury	Cinnabar, HgS	Direct reduction of HgS by heat alone
· · · · ·		$HgS + O_2 \longrightarrow Hg + SO_2$

### 4.9 FURNACES

Furnace is a device in which high temperature is produced either by burning a fuel or by using electricity. Several types of furnaces are used in the extraction of metals. The important ones are described below:

#### 38 (i) Reverberatory Furnace

This is the kind of a furnace in which fuel does not come in direct contact with the charge. The flames are deflected

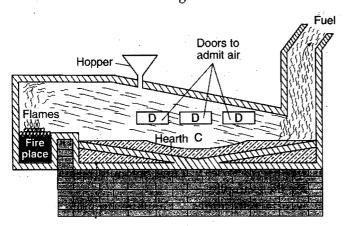


Fig. 4.17 Reverberatory furnace

from the roof of the furnace to the charge undergoing reaction. Thus, this furnace can be used for reduction as well as for oxidation purposes.

The furnace consists of three main parts namely fire place, hearth and chimney. The fire place is built at one end of the furnace at slightly lower level than that of the hearth. The roof is made slanting and connects with the chimney on the other end. The hot gases from the fire place are reflected by the concave ceiling over the hearth. The furnace is surrounded on all sides by walls of fire bricks. Air supply can be controlled by vents and direct blast.

The furnace is used for smelting (reduction) and roasting of the ores. The reduction is done by the use of some suitable reducing agent. The furnace is used (a) for reducing the roasted tin stone  $(SnO_2)$  to molten tin metal by the use of coke, (b) for roasting the galena ore (PbS) as to convert it into PbO and PbSO<sub>4</sub> by the use of air, (c) for roasting of copper pyrites  $(CuFeS_2)$  as to convert it into  $Cu_2O$  and FeO by means of air.

#### (ii) Blast Furnace

Iron ore is converted to iron in a special type furnace, called **blast furnace** (fig. 4.18). It is a huge chimney like structure which can be between 25 and 60 metres in height and 5 to 10 metres in diameter. It is constructed of steel plates

and the inner regions lined with fire-bricks. It has a double cup and cone arrangement at the top for the introduction of charge. Preheated air at a temperature of about 600°C is injected into the furnace through a number of pipes called tuyeres in the bottom of the furnace. It is provided with two tap holes plugged with clay; molten metal is tapped from the lower one and molten slag from the other. The temperature range in the furnace is from 1600°C at the bottom and 200–300°C at the top. Carbon and carbon monoxide reduce the metallic oxides to the free metals.

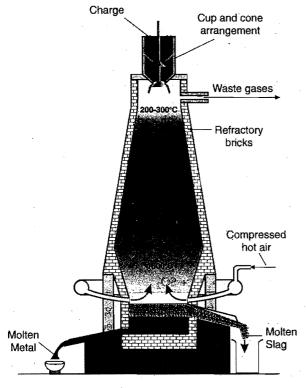


Fig. 4.18 Blast furnace

Blast furnace is frequently used for the extraction of iron and copper from their ores. Slag formation plays an important role in the blast furnace as it covers the melted metal and thus protects the metal from being reoxidised.

#### (iii) Muffle Furnace

This furnace is used when high temperature is required and the fuel and its products of combustion are not to be desired to come into contact with the material to be heated. The muffle is a chamber made of refractory material. The muffle is surrounded by hot flames and hot gases all

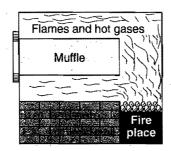


Fig. 4.19 Muffle furnace

around. In an electric muffle furnace the closed chamber is surrounded by heating electric coils. Such a furnace is used for the extraction of zinc, for annealing of gold and silver assaying.

#### (iv) Electric Furnaces

In these furnaces, electrical energy is converted into heat energy. Such furnaces are largely used where cheap power is available and very high temperatures are required and also for carrying electrolytic reduction. The electric furnaces are generally of three types:

- (a) Induction furnace,
- (b) Arc furnaces and
- (c) Resistance furnace.
- (a) Induction furnace: In this furnace the charge lying on the furnace bed or in a crucible constitute the secondary coil of an induction unit and the induced currents produced by making and breaking the primary circuit, heat up the material.
- **(b) Arc furnaces :** Heat is generated by arcs and a temperature over 3000°C may be obtained. Carbon electrodes are used to carry the current and an arc is struck between them and the charge. Arc furnaces are of two types:
  - (i) Direct heat and
  - (ii) Indirect heat.

In the direct heat arc furnaces, arc is used to heat up a gas in which the arc is burning and in indirect heat arc furnace, the arc burns above the charge, *i.e.*, the arc radiates heat towards the charge.

(c) Resistance furnace: Heat is generated by the resistance in the electric circuit. In some cases the material forming the charge may act as the resistance and in other cases, the body of furnace is made up of resistance material and this material cause heating. In some cases, rods of poorly conducting materials are embedded into the charge which become intensely hot on passage of the current.

### 4.10 REFRACTORY MATERIALS

The materials which can withstand very high temperatures without melting or becoming soft are known as refractory materials. These are not affected by slags formed during the extraction of metals. These are used in the form of bricks for the internal linings of furnaces. Refractory materials used are of three types:

- (i) Acid refractories: Silica, quartz, silicious sand stones, etc., are the examples.
- (ii) Basic refractories: Lime, dolomite, magnesite, etc., are the examples.
- (iii) Neutral refractories: Graphite, chromite, bone ash, etc., are the examples.

Silica (92% SiO2, 2.7% Al2O3) and quartz can tolerate

temperatures upto about 1750°C, bauxite upto 1800°C, alumina upto 2000°C and magnesite, chromite, etc., upto

2200°C. Some carbides such as silicon carbide is used as refractory for special purposes.

### MINERAL RESOURCES OF INDIA

Mineral resources of a country determine the economic position of the country. The country which is rich in mineral resources is definitely a prosperous country. India has large mineral resources but not too large in view of the country's huge size and population. India has abundant reserves of coal, mica ore, manganese ore, iron ore, aluminium ore, titanium ore, etc., but particularly poor in non-ferrous metals. A short description of the important metals found in India is given here.

- 1. Iron: India contains some of the world's largest reserves of iron ore, mainly haematite and magnetite. India holds the sixth position regarding the production of iron ore in the world. Large deposits have been reported in Bihar, Jharkhand, Orissa, Madhya Pradesh, Karnataka, Andhra Pradesh and Goa. The states of Orissa and Jharkhand [Singhbhum (Jharkhand); Keonjhar, Sonai and Mayurbhanj (Orissa)] produce over 75% of the total iron ore produced in India. The important steel plants are located at Bhilai, Durgapur, Rourkela, Jamshedpur, Bhadravati and Burnpur.
- Manganese: India possesses large reserves of manganese ore mainly pyrolusite (MnO<sub>2</sub>). India holds the fourth position in the production of manganese ore in the world. Orissa is the leading producer followed by Karnataka, Madhya Pradesh and Maharashtra.
- 3. Aluminium: India is rich in bauxite reserves. Workable deposits are found in Jharkhand, Madhya Pradesh, Tamil Nadu, Maharashtra, Karnataka, Orissa and Gujarat. The availability of cheap power is a must

- for the development of aluminium industry in India.
- 4. Copper: The known copper ore deposits in India are meagre. Almost all the present production of copper ore comes from Singhbhum and Hazaribagh districts of Jharkhand and Khetri of Rajasthan
- 5. Gold: India has very meagre gold reserves. The only gold mine is at Kolar in Karnataka state. It is one of the deepest mines of the world.
- Chromium: Chromite (FeO Cr<sub>2</sub>O<sub>3</sub>) is the chief ore of chromium. It is mainly found in Orissa, Jharkhand, Mysore and Maharashtra.
- 7. **Barium:** Barytes is the main ore of barium. It is mainly found in Andhra Pradesh, Rajasthan and Tamil Nadu.
- 8. Lead and Zinc: India has no important deposits of lead and zinc ores. Recently lead and zinc ores have been found at Zawar mines near Udaipur and at Hazaribagh (Jharkhand). Zawar deposits contain 8–10% Zn and 5% lead.
- Calcium: The sulphate ore of calcium (gypsum) is mainly found in Rajasthan. Limestone and marble (calcium carbonate) are found in large amounts in almost all the states of India.
- 10. Titanium: The principal ore of titanium is ilmenite. It is mainly found in the eastern and western coasts of India.
- Thorium: Beach sands of Kerala and Tamil Nadu contain a useful mineral monazite which is used for the extraction of thorium and rare-earths.

### SOME SOLVED PROBLEMS

**Problem 1.** What are four most abundant elements in earth's crust? Arrange them in decreasing abundance.

#### Solution:

Oxygen, silicon, aluminium and iron are the most abundant elements in the earth's crust. The abundance order is:

#### O > Si > Al > Fe

**Problem 2.** In general which metal do you expect to occur in the native state in nature? Give examples.

#### Solution:

The metals which are below hydrogen in the electrochemical series, *i.e.*, which are less electropositive metals can occur in native state in nature. These metals are not readily attacked by oxygen, moisture, carbon dioxide, etc. Examples are: Ag, Au, Pt, Pd, etc. **Problem 3.** Why do metal sulphides occur mainly in rocks and metal halides in lakes and seas?

#### Solution:

Metal sulphides are insoluble in water while metal chlorides are soluble in water. Thus, chlorides get dissolved in rain water and washed away to lakes and seas.

**Problem 4.** What is the role of depressant in froth floatation process?

#### Solution:

The depressants help in the separation of two sulphide ores. For example, in case of an ore containing PbS (Galena) and ZnS (Zinc blende), the depressant is NaCN. It prevents ZnS from coming to the froth but allows PbS to come with froth in the froth floatation process. ZnS forms a soluble complex with NaCN.

$$ZnS + 4NaCN \longrightarrow Na_2Zn(CN)_4 + Na_2S$$
  
Sodium tetracyanozincate (II)

**Problem 5.** What is the significance of leaching in the extraction of aluminium?

#### Solution:

The bauxite ore is always associated with silica, iron oxide and titanium oxide as impurities. These impurities are removed by the process of leaching. The powdered bauxite ore is heated with 45% solution of NaOH at 473–523 K. Alumina and silica dissolve while Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> remain insoluble. These are filtered off and solution is neutralised with CO<sub>2</sub> and freshly precipitated Al(OH)<sub>3</sub> is added when hydrated alumina separates out. The sodium silicate remains in solution. Hydrated alumina is separated and dried. This gives pure alumina on heating strongly.

$$\begin{array}{c} \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} + \text{H}_2\text{O} \xrightarrow{473-523 \text{ K}} 2\text{Na[Al(OH)}_4] \\ \text{Bauxite} & \text{Sod. aluminate} \\ \text{SiO}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SiO}_3 \\ \text{Sod. silicate} \\ 2\text{Na[Al(OH)}_4] + 2\text{CO}_2 \longrightarrow \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 2\text{NaHCO}_3 + \text{H}_2\text{O} \\ \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \xrightarrow{1473 \text{ K}} \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O} \end{array}$$

**Problem 6.** Which of the ores can be concentrated by magnetic separation?

#### Solution:

The ores in which one of the components either the actual ore or the impurity is magnetic in nature can be concentrated by magnetic separation. For example, ores of iron such as haematite, magnetite, siderite, etc., can be concentrated by magnetic separation.

**Problem 7.** Differentiate between

- (i) Minerals and ores
- (ii) Roasting and calcination.

#### **Solution:**

(i) The natural substances in which metals occur in the earth are called **minerals**. The mineral has a definite composition. It may be a single compound or a complex mixture. It is usually associated with a number of impurities.

The minerals from which the metals can be conveniently and economically extracted are known as **ores**.

Thus, all ores are minerals but all minerals are not ores.

For example, iron is found in the nature as oxides, carbonate and sulphides. Out of these minerals, the oxides of iron such as haematite, magnetite, etc., are used for extraction. Therefore, oxides of iron are the ores of iron.

- (ii) Calcination is a process in which the ore is heated below its fusion temperature in absence of air. The process does the following things:
  - (a) It removes the volatile impurities like CO<sub>2</sub>, SO<sub>2</sub> organic matter, moisture from the ore.
  - (b) It removes water from hydrated oxide ore.

$$Al_2O_3 \cdot 2H_2O \longrightarrow Al_2O_3 + 2H_2O$$
  
 $2Fe_2O_3 \cdot 3H_2O \longrightarrow 2Fe_2O_3 + 3H_2O$ 

(c) It removes CO<sub>2</sub> from a carbonate ore.

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CuCO_3$$
·  $Cu(OH)_2 \longrightarrow 2CuO + CO_2 + H_2O$ 

This process is generally done in a reverberatory furnace. This process makes the ore porous.

Roasting is a process in which the ore (usually the sulphide ore) is heated strongly in the presence of excess of air. The heating should be done at a temperature below the melting point of the ore. The ore is heated alone or mixed with some other materials. The process does the following things.

- (a) It dries the ore.
- (b) The volatile impurities like CO<sub>2</sub>, SO<sub>2</sub> organic matter, moisture are all driven out.
- (c) The ore is converted into oxide.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$
  
 $2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$ 

Sometimes sulphide ore is converted into sulphate.

$$PbS + 2O_2 \longrightarrow PbSO_4$$

(d) The sulphide ore is converted into chloride.

$$Ag_2S + 2NaCl \longrightarrow 2AgCl + Na_2S$$

**Problem 8.** Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction?

#### Solution:

The entropy of a substance is higher in liquid state than in solid state. In the reduction of a metal oxide, the entropy change ( $\Delta S$ ) will be +ve if the metal formed is in liquid state. Thus, the value of  $\Delta G^{\circ}$  becomes negative and reduction occurs easily.

**Problem 9.** Out of C and CO which is a better reducing agent at 673K?

#### Solution:

When carbon acts as a reducing agent, it is either converted into CO or  $CO_2$  or both.

$$2C + O_2 \longrightarrow 2CO$$
$$C + O_2 \longrightarrow CO_2$$

CO is oxidised to CO<sub>2</sub> when it is used as a reducing agent.

$$2CO + O_2 \longrightarrow 2CO_2$$

From the Ellingham diagram, it is clear that at the temperature 673 K, the  $\Delta G^{\circ}$  of the formation of  $CO_2$  from CO is more negative than the formation of CO or  $CO_2$  from carbon. Hence, at temperature 673 K, CO is a better reducing agent than C.

**Problem 10.** Out of C and CO, which is a better reducing agent for ZnO?

#### Solution:

From the Ellingham diagram, it is clear that the free energy of formation of CO from C is lower at temperatures above 1120 K while that of CO<sub>2</sub> from carbon is lower above

1323 K than free energy of formation of ZnO. However, the free energy of formation of CO<sub>2</sub> from CO is always higher than that of ZnO. Hence, C is a better reducing agent of ZnO.

**Problem 11.** The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with two examples.

#### Solution:

From the Ellingham diagram, it is evident that any metal oxide with lower  $\Delta G^{\circ}$  is more stable than the metal oxide with higher  $\Delta G^{\circ}$ . This implies that the metal oxide placed lower in the diagram cannot be reduced by the metal involved in the formation of the oxide placed higher in the diagram. However, reverse can readily take place. Thus,  $Al_2O_3$  cannot be reduced by Cr. However, chromium oxide can be reduced by Al.

At temperature 1773 K, the change in free energy for the formation of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> is given below:

$$2Al + \frac{3}{2}Q_2 \longrightarrow Al_2O_3$$
;  $\Delta G = -900 \text{ kJ mol}^{-1}$  ... (i)  
 $2Cr + \frac{3}{2}Q_2 \longrightarrow Cr_2O_3$ ;  $\Delta G = -500 \text{ kJ mol}^{-1}$  ... (ii)

The reaction for the reduction of Al<sub>2</sub>O<sub>3</sub> with Cr may be obtained by subtracting eq. (i) from eq. (ii).

$$Al_2O_3 + 2Cr \longrightarrow Cr_2O_3 + 2Al; \quad \Delta G = 400 \text{ kJ mol}^{-1}$$

This reaction is thermodynamically not feasible since  $\Delta G$  has +ve value.

The reaction for the reduction of Cr<sub>2</sub>O<sub>3</sub> with Al may be obtained by subtracting eq. (ii) from eq. (i).

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr; \quad \Delta G = -400 \text{ kJ mol}^{-1}$$

This reaction is feasible since  $\Delta G$  has negative value. Similarly, both Al and Zn can reduce FeO to Fe but Fe cannot reduce Al<sub>2</sub>O<sub>3</sub> or ZnO.

Thus, thermodynamic factor helps in choosing a suitable reducing agent for the reduction of a particular metal oxide.

**Problem 12.** (i) Suggest a condition under which magnesium could reduce alumina.

(ii) Predict condition under which Al might be expected to reduce MgO.

#### Solution:

- (i)  $\Delta G$  of formation of Al<sub>2</sub>O<sub>3</sub> at temperatures below 1665 K is less negative than  $\Delta G$  of formation of MgO. Thus, below 1665 K magnesium can reduce Al<sub>2</sub>O<sub>3</sub> to Al.
- (ii) The temperature of intersection of the Al  $\longrightarrow$  Al<sub>2</sub>O<sub>3</sub> and Mg  $\longrightarrow$  MgO curves in the Ellingham diagram is 1665 K. Above this temperature,  $\Delta G$  of formation of Al<sub>2</sub>O<sub>3</sub> is more negative than  $\Delta G$  of formation of MgO. Thus, above 1665 K aluminium can reduce MgO into Mg.

**Problem 13.** Copper can be extracted by hydrometallurgy but not zinc. Explain.

#### Solution:

Copper is comparatively less active metal as its reduction potential, *i.e.*,  $E^{\circ}(Cu^{2+}/Cu)$  is high (+ 0.34 V). It can be displaced from solutions of  $Cu^{2+}$  ions by more active metals which have  $E^{\circ}$  values lower than copper. For example,  $E^{\circ}$  of zinc  $(Zn^{2+}/Zn)$  is -0.76 V and thus, zinc can displace copper from solutions of  $Cu^{2+}$  ions.

In contrast to displace zinc from solutions of  $Zn^{2+}$  ions a more reactive metal than it is required. But, the more active metals readily react with water forming their corresponding ions and evolve hydrogen gas. Thus, it is difficult to displace zinc from solutions of  $Zn^{2+}$  ions. Hence, copper can be extracted by hydrometallurgy but not zinc.

# SUMMARY AND IMPORTANT POINTS TO REMEMBER



- The most abundant element in the earth's crust is oxygen. Next to oxygen is the element silicon.
- 2. The most abundant metal in the earth's crust is aluminium.
- The most abundant transition metal in the earth's crust is iron.
- 4. About 88 elements are naturally occurring while the remaining have been synthesized. The earth's crust is the biggest source of metals. Metals occur in nature sometimes free (native state) but mostly in the combined state. The natural substances in which the metals or their compounds occur in the earth are called minerals. The minerals from which the metal can be conveniently and economically extracted are called ores. Ores may be divided into four groups:
  - (a) Native ores: Metals present in free state associated with rock or alluvial materials such as gold, platinum, silver, etc. Sometimes lumps of pure metals are found. These are termed nuggets.

- (b) Sulphurised or arsenical ores: The examples are: Galena (PbS); Zinc blende (ZnS); Cinnabar (HgS); Argentite (Ag<sub>2</sub>S); Copper pyrite (CuFeS<sub>2</sub>); Kupfer nickel (NiAs).
- (c) Oxidised ores: Metals are present as oxides or oxysalts. The examples are: Haematite (Fe<sub>2</sub>O<sub>3</sub>); Bauxite (Al<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O); Tinstone (SnO<sub>2</sub>); Rutile (TiO<sub>2</sub>); Zincite (ZnO); Limestone (CaCO<sub>3</sub>); Dolomite (CaCO<sub>3</sub>· MgCO<sub>3</sub>); Malachite [CuCO<sub>3</sub>· Cu(OH)<sub>2</sub>]; Calamine (ZnCO<sub>3</sub>); Chile saltpetre (NaNO<sub>3</sub>); Gypsum (CaSO<sub>4</sub>· 2H<sub>2</sub>O); Barytes (BaSO<sub>4</sub>); Beryl (3BeO· Al<sub>2</sub>O<sub>3</sub>· 6SiO<sub>2</sub>).
- (d) Halide ores : Examples are : Common salt (NaCl); Carnallite (KCl·MgCl $_2$ ·6H $_2$ O), Fluorspar (CaF $_2$ ).
- 5. The whole process of obtaining a pure metal from one of its ores is known as metallurgy. Metallurgy of a metal involves three main operations:
  - (a) Concentration or dressing of the ore (b) Isolation of crude metals (c) Purification or refining.

- 6. The undesired impurities such as sand, clay, rocks, etc., associated with the ore are called gangue or matrix. The removal of these impurities from the ores is known as concentration or dressing of ores. The concentration is done in a number of ways depending upon the nature of impurities.
  - (a) The process of removing the lighter particles of sand, clay, etc., by washing with water either using Wilfley table or Hydraulic classifier is called levigation or gravity separation.
    - The oxide ores of iron (haematite) and tin (cassiterite or tinstone) and native ores of Ag, Au, etc., are concentrated by this process.
  - (b) Electromagnetic separation method is applied when either the ore or the impurities are magnetic in nature. Chromite ore (magnetic) is separated from non-magnetic silicious impurities. Wolframite (FeWO<sub>4</sub>), a magnetic ore is separated from non-magnetic ore, cassiterite (SnO<sub>2</sub>), by this method.
  - (c) Froth floatation process is used for the concentration of sulphide ores. This process is based on the preferential wetting of ore particles by oil (pine oil) and gangue particles by water. Zinc blende, copper pyrites, galena, etc., are concentrated by this process.
  - (d) Leaching involves the treatment of the ore with a suitable reagent to make it soluble while impurities remain insoluble. The ore or the metal is recovered from the solution by a suitable chemical method.
    - For example, bauxite is digested with aqueous solution of NaOH, when  $Al_2O_3$  dissolves forming sodium meta aluminate (NaAlO<sub>2</sub>) while impurities such as  $Fe_2O_3$ ,  $TiO_2$  and silica remain insoluble. Pure alumina is recovered from the filtrate.
    - Native ores of Ag and Au are treated with aqueous dilute solution of NaCN in presence of oxygen. The Ag and Au particles get dissolved forming complex cyanides. Ag or Au is recovered from the solution by addition of electropositive metal, Zn.
- 7. Extraction of crude metals: Metals are usually extracted by reduction. Thus, the concentrated ore is converted into a form which is suitable for reduction. Oxides are easier to reduce. Therefore, the extraction involves the following two steps:
  - (a) Conversion of the ore into metallic oxide.
  - (b) Reduction of metallic oxide.
  - (a) Two methods are used for conversion into oxides.
    - (i) Calcination involves heating of the ore below its fusion temperature in absence of air. This step expels organic matter and moisture from the ores. Carbonates may be decomposed.
    - (ii) Roasting involves heating of the ore either alone or with some other material in presence of oxygen (air) below its fusion temperature. This process is generally done in a reverberatory furnace. Nonmetallic impurities are removed as their volatile oxides. The ores such as sulphides are simultaneously converted into corresponding oxides either partially or completely.
  - (b) Reduction of the oxide to the free metal is done by a suitable reducing agent. The following methods can be applied.

- (i) Smelting: The process of extracting a metal by heating the metal oxide with a suitable reducing agent such as C, H<sub>2</sub>, CO, water gas, Na, K, Mg, Al, etc., at high temperature is called smelting. The process, in general, is termed pyrometallurgy. It is applicable especially for the extraction of less electropositive metals such as Fe, Zn, Pb, Sn, etc., carbon, carbon monoxide and aluminium are generally used as reducing agents.
  - The term smelting is applied when coke or carbon is used as a reducing agent. The ore is mixed with a suitable quantity of coke or charcoal (acts as a reducing agent) and heated to a high temperature above its melting point. An additional reagent is usually added to the concentrated ore to remove if still impurities are present. This additional reagent is called flux. Flux combines with impurities and forms a fusible slag. The selection of flux depends on the nature of impurities. If impurities are acidic, basic flux such as CaO is used while acidic flux such as silica is used if the impurities are basic. The process is carried out in a blast furnace.
- (ii) Goldschmidt aluminothermic process—Reduction by aluminium: This process is used in the case of those metals which have very high melting points and are to be extracted from their oxides. A mixture of metal oxide and aluminium powder, commonly called as thermite, is taken in a steel crucible placed in a bed of sand. The reaction is started by the use of an ignition mixture containing magnesium powder and barium peroxide.
- (iii) Auto or Self reduction process: The sulphide ores of less electropositive metals like Hg, Pb, Cu, etc., are heated in air as to convert part of the ore into oxide or sulphate which then reacts with the remaining sulphide ore to give the metal and SO<sub>2</sub>. No external reducing agent is used in this process.
- (iv) Electrolytic reduction: The highly electropositive metals such as alkali metals, alkaline earth metals, Al, etc., are extracted by the electrolysis of hydroxides, chlorides or oxides in the fused state. Sometimes, a small amount of some other salt is added to decreases the fusion temperature or to increase the conductivity or both. The metal is liberated at the cathode.
- (v) Hydrometallurgy: Certain metals such as silver and gold are extracted by dissolving the concentrated ore in some suitable reagent and then recovering the metal from the solution by treatment with some more electropositive metal.
- 8. Thermodynamic principles: The basic concepts of thermodynamics are quite helpful in selecting a suitable reducing agent for a particular oxide. In the oxidation reduction reaction, the Gibbs free energy change should be negative at an appropriate temperature.

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

The concept is graphically displayed in plots of  $\Delta G^{\circ}$  vs T (Ellingham diagram). Any metal oxide with lower value of  $\Delta G^{\circ}$  is more stable than metal oxide with higher  $\Delta G^{\circ}$ . This implies that metal oxide placed higher in the diagram can

be reduced by the metal involved in the formation of the oxide placed lower in the diagram. This concept is applied in the extraction of Fe, Zn and Cu.

9. The concept of electrode potential is useful in the isolation of the metals either by electrolysis or by displacing one metal by other in the solution. The sum of the E° of two redox couples should be positive so that Gibbs energy change is negative.

$$\Delta G^{\circ} = -nFE^{\circ}$$

The process of extraction of metals by electrolysis of their fused salts is called electrometallurgy. In electrolysis, electrons act as reducing agent at cathode. One example of the electrometallurgy is the extraction of aluminium metal from bauxite ore.

- Third operation: Purification or refining: The process of purifying impure metals is called refining.
  - (a) Liquation process: The process is based on the difference in fusibility of the metal and impurities. When the impurities are less fusible than the metal itself, this process is used. The impure metal such as Bi, Sn, Pb, Hg, etc., is placed on the sloping hearth of a furnace and gently heated. The metal melts and flows down.
  - (b) Distillation: The process is used for those metals which are volatile. The impure metal is heated and the vapours are separately condensed in a receiver. This is used for the purification of Zn, Cd, Hg, etc.
  - (c) Cupellation: The impure metal is heated in cupel or oval shaped crucible made of bone ash or cement and a blast of air is passed over the molten mass. The impurities are oxidised and removed with the blast of air. Impurity of lead in silver is removed by this process.
  - (d) Poling: It is used for purification of those metals which contain their own oxides as impurity. The molten impure metal is stirred with green poles of wood.
  - (e) Electrorefining: Metals like Cu, Ag, Au, Ni, Cr, Al, etc., are purified by this method. The impure metal is made the anode and a strip of pure metal is made as cathode while electrolytic solution consists of a solution of a suitable salt of the metal.
  - (f) Zone refining: When highly pure metals are required, this method is applied for purification. The method is based on the difference in solubility of impurities in molten and solid state of the metal. This method is used in purification of germanium, gallium, silicon, etc., which are used as semiconductors.
  - (g) Van Arkel process: This method is used for obtaining ultrapure metals. The impure metal is converted into volatile compound which is then decomposed electrically to get pure metal. Ti, Zr, Hf, Si, etc., are refined by this method.

$$\begin{array}{ccc} \text{Impure} & + \text{ } I_2 \rightarrow \text{Metal iodide} & \xrightarrow[\text{flament}]{\text{Heating}} & \text{Metal} & + \text{ } I_2 \\ \text{metal} & & & \text{vapours} & & \text{flament} \end{array}$$

**(h) Mond's process:** Nickel is purified by this method. The impure nickel is treated with CO at 330–350 K, when

volatile nickel carbonyl is formed. The carbonyl is subjected to 450-470 K, when it decomposes giving pure nickel.

Impure + CO 
$$\xrightarrow{330-350 \text{ K}}$$
 NiCO<sub>4</sub>  $\xrightarrow{450-470 \text{ K}}$  Ni + 4CO nickel  $\xrightarrow{\text{Volatile}}$  compound

- (i) Chromatographic methods: It is based on selective distribution of various constituents of a mixture between two phases, a stationary phase and a moving phase. The stationary phase can be either solid or tightly bound liquid on a solid support. The moving phase may be a liquid or a gas. Different types of chromatographic methods have been developed. The most common are:
  - (a) Column chromatography,
  - (b) Thin layer chromatography,
  - (c) Paper chromatography,
  - (d) Gas chromatography, etc.

Column chromatography is the simplest method. This is based on adsorption phenomenon. The extent of adsorption of various constituents present in the mixture liquid (moving phase) varies with a given adsorbent (stationary phase). The common adsorbents used are alumina, silica gel, magnesium oxide, active animal charcoal, etc.

It involves the following steps:

- (a) Preparation of adsorption column
- (b) Adsorption
- (c) Elution of components and recovery.

This method is useful for those elements which are available in small amounts and the impurities are not much different in chemical properties from the element to be purified.

- 11. The materials which can withstand very high temperatures without melting or becoming soft are known as refractory materials. These are used in the form of bricks for the internal linings of furnaces. Silica, quartz, lime, graphite, bone ash, etc., are used as refractory materials. Refractory materials are of three types:
  - (i) Acid refractories: Silica, quartz, silicious sand stones, etc., are the examples.
  - (ii) Basic refractories: Lime, dolomite, magnesite, etc., are the examples.
  - (iii) Natural refractories: Graphite, chromite, bone ash, etc., are the examples.

Silica (92% SiO<sub>2</sub>, 2.7% Al<sub>2</sub>O<sub>3</sub>) and quartz can tolerate temperatures upto about 1750°C, bauxite upto 1800°C, alumina upto 2000°C and magnesite, chromite, etc., upto 2200°C. Some carbides such as silicon carbide is used as refractory for special purposes.

12. India has abundant reserves of coal, mica ore, manganese ore, iron ore, aluminium ore, titanium ore, etc., but particularly poor in non-ferrous metals.

## -•••- PRACTICE PROBLEMS -•••-

#### **■** Subjective Type Questions

- 1. (a) Name one oxide ore of each of the following metals :
  - (i) iron (ii) zinc (iii) aluminium
  - (b) Name the metal present in :
    - (i) chlorophyll (ii) haemoglobin
- 2. (a) What types of ores are roasted?
  - (b) How is copper pyrite concentrated?
  - (c) How is bauxite generally concentrated?
- (a) Name the diagram which can be used to compare the reducing nature of different elements.
  - (b) Indicate the temperature at which carbon can be used as reducing agent for FeO.
  - (c) Which is a better reducing agent below 983 K, Carbon or carbon monoxide?

#### 4. Name the following:

- (i) Two metals which never occur in native state.
- (ii) Two metals which always occur both in native and in combined states.
- (iii) Two metals which always occur naturally in an uncombined state.
- (iv) Two metals which are manufactured by the electrolysis of their fused salts.
- (v) Two metals which are used for the reduction in metallurgical process.
- **5.** Name the metals with which the following ores/minerals are associated :
  - (i) Cryolite
- (ii) Dolomite (iii) Calamine
- (iv) Haematite
- (v) Malachite (vi) Lepidolite
- (vii) Polyhalide (viii) Triphylite (ix) Borax (x) Chromite
- 6. What term is assigned to the following?
  - (i) Naturally occurring compounds from which metals are extracted profitably.
  - (ii) Sulphide ores are generally heated in a stream of air.
  - (iii) Metal is extracted from its ore by heating the ore with a suitable reducing agent.
  - (iv) Metal ions get discharged on an electrode.
  - (v) The materials which can withstand very high temperatures without melting and softening.
  - (vi) The substances used for the removal of gangue in the ores in the form of slags.
  - (vii) The process in which aluminium is used as a reducing agent for the extraction of metal from its oxide.
- 7. Differentiate the following giving a suitable example :
  - (i) Mineral and ore
  - (ii) Calcination and roasting
  - (iii) Flux and slag
  - (iv) Smelting and roasting-
- 8. Write short notes on:
  - (i) Froth floatation process (ii) Calcination
  - (iii) Roasting
- (iv) Smelting
- (v) Hydrometallurgy
- (vi) Pyrometallurgy

- (vii) Autoreduction
- (viii) Electrolytic refining
- (ix) Reverberatory furnace
- (x) Blast furnace
- (xi) Leaching
- (xii) Cupellation
- 9. (a) Which of the following metals can be obtained by the electrolytic reduction of aqueous solution of their salts— Al, Na, Cu and Ag?
  - (b) Which of the metals Na, Ag and Fe are extracted by,
    - (i) Complex formation
    - (ii) Reduction with carbon and
    - (iii) Electrolysis of fused salt?
  - (c) Which ores are generally concentrated by froth floatation process?
  - (d) (i) Which of the following metals is lightest and which one of them is least reactive?

(ii) Which one out of the two may be found in native state?

#### 10. Explain the following:

(i) Zinc but not copper is used for the recovery of Ag from the complex [Ag(CN)<sub>2</sub>]<sup>-</sup>.

[Hint: Zinc is more powerful reducing agent in comparison to copper. Zinc is also cheaper than copper.]

(ii) Partial roasting of sulphide ore is done in the metallurgy of copper.

[Hint: Partial roasting of sulphide ore forms some oxide.

This oxide then reduces the remaining sulphide ore into metal.

$$2CuS + 3O_2 \longrightarrow 2CuO + 2SO_2$$

$$2CuO + CuS \longrightarrow 3Cu + SO_2$$
 (Autoreduction) ]

(iii) Why is chalcocite roasted and not calcined during recovery of copper?

[Hint: Chalcocite is a sulphide ore. It is to be converted into oxide and thus roasting and not calcination is done.]

(iv) Aluminium metal is frequently used as a reducing agent for the extraction of metals such as chromium, manganese, etc.

[Hint: Aluminium has great affinity for oxygen. It acts as a reducing agent when the metal having high melting point is to be extracted from its oxide.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$

(v) Magnesium oxide is used for the lining in steel making furnace.

[Hint: Magnesium oxide acts as a flux to remove impurities of Si, P and S through slag formation.

$$\begin{array}{c} MgO + SiO_2 \longrightarrow MgSiO_3 \\ 3MgO + P_2O_5 \longrightarrow Mg_3(PO_4)_2 \\ MgO + SO_2 \longrightarrow MgSO_3 \end{array} \end{array} \} Slag I$$

- 11. How the following impurities can be removed?
  - (a) An impurity of lead in silver.
  - (b) An impurity of cuprous oxide in copper.
  - (c) Impurities of Fe, Cu, etc., in aluminium.
- **12.** Describe the thermodynamic principles of metallurgy. How Ellingham diagram is useful in predicting the feasibility of thermal reduction of a metal oxide.
- 13. Describe the principle of extraction of each of the following:(a) Cu from CuFeS<sub>2</sub> (b) Zn from ZnO (c) Fe from Fe<sub>2</sub>O<sub>3</sub>
- 14. Explain the following:
  - (a) Carbon reduction process is not applied for reducing alumina.
  - (b) Aqueous solution of sodium chloride cannot be used for the isolation of sodium by electrolysis.
  - (c) Graphite is used as anode and not diamond.

#### ■ Matching Type Questions

#### Match the following:

[A] (a) Al	(i)	Cinnabar
(b) Cu	(ii)	Calamine
(c) Mg	(iii)	Cryolite
(d) Zn	(iv)	Malachite
(e) Hg	(v)	Carnallite

[B]	(a) Zn	(i) Self reduction
	(b) Ag	(ii) Fused salt electrolysis
	(c) Fe	(iii) Carbon reduction
	(d) Ca	(iv) Amalgamation
	(e) Cu	(v) CO reduction

(i) PbS
(ii) KCl·MgCl <sub>2</sub> ·6H <sub>2</sub> O
(iii) Al <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O
(iv) SnO <sub>2</sub>
(v) ZnCO <sub>3</sub>
(i) Silver
(iii) Al <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O (iv) SnO <sub>2</sub> (v) ZnCO <sub>3</sub>

(b) Mona's process	(11) Iron
(c) Cupellation	(iii) Carbonate ores
(d) Calcination	(iv) Froth floatation proces
(e) Pyrometallurgy	(v) Nickel

### Answers

#### Answers: Subjective Type Questions

- 1. (a) (i) Haematite (ii) Zincite (iii) Bauxite
  - (b) (i) Magnesium (ii) Iron
- 2. (a) sulphide ores (b) froth floatation process (c) leaching
- 3. (a) Ellingham diagram (b) Above 1123 K (c) Carbon monoxide
- (i) Sodium and potassium; (ii) Copper, silver; (iii) Au, Pt; (iv) Sodium, aluminium; (v) Aluminium, magnesium, iron or sodium.
- 5. (i) Na and Al; (ii) Mg and Ca; (iii) Zn; (iv) Fe; (v) Cu; (vi) Li, Al, Na and K; (vii) K, Mg and Ca; (viii) Li, Na, Fe and Mn; (ix) Na; (x) Cr, Fe.
- (i) ores, (ii) roasting, (iii) smelting, (iv) electrolytic reduction,
   (v) refractory materials, (vi) fluxes, (vii) thermite process.
- (a) Cu and Ag; (b) (i) Ag, (ii) Fe, (iii) Na; (c) Sulphide ores; (d) (i) lightest element Al, least reactive Ag, (ii) Ag.
- 11. (a) Cupellation, (b) Poling, (c) Electrolytic.

#### Answers: Matching Type Questions

(A) (a—iii); (b—iv); (c—v); (d—ii); (e—i) (B) (a—iii); (b—iv); (c—v); (d—ii); (e—i) (C) (a—v); (b—i); (c—iv); (d—iii); (e—ii) (D) (a—iv); (b—v); (c—i); (d—iii); (e—ii)

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS



1. The main ore of lead is galena (PbS). Lead is extracted from galena ore either by (A) or (B).

(A) PbS 
$$\xrightarrow{\text{Roasted}}$$
 PbO + SO<sub>2</sub>

Heated with C  $\rightarrow$  Pb + CO<sub>2</sub>

(B) PbS  $\xrightarrow{\text{Roasted}}$  PbO + PbS

(B) PbS 
$$\xrightarrow{\text{Roasted}}$$
 PbO + PbS

Heated with PbS Pb + SO<sub>2</sub>

Auto-reduction process is:

- (b) B (a) A
- (c) both
- (d) none

Which of the following processes involves smelting?

(a) 
$$ZnCO_3 \xrightarrow{Heat} ZnO + CO_2$$

(b) 
$$2PbS + 3O_2 \xrightarrow{\text{Heat}} 2PbO + 2SO_2$$

(c) 
$$Al_2O_3 \cdot 2H_2O \xrightarrow{Heat} Al_2O_3 + 2H_2O$$

(d) 
$$Fe_2O_3 + 3C \xrightarrow{Heat} 2Fe + 3CO$$

Ans. (d)

- Consider the following statements:
  - Roasting is carried out to:
  - 1. convert sulphide into oxide
  - 2. melt the ore
  - 3. remove moisture, water of hydration and expel organic
  - 4. remove sulphur and arsenic in the form of volatile oxides

Out of these statements:

- (a) 1, 3 and 4 are correct
- (b) 1, 2 and 3 are correct
- (c) 2, 3 and 4 are correct
- (d) 1, 2 and 4 are correct

Ans. (a)

4. Match List I with List II and select the correct answer using the codes given ahead:

#### List I

- A. Mond's process 1. Purification of copper
- B. Van Arkel method
- C. Cupellation
- D. Distillation

#### Codes:

- (a) A-1, B-2, C-3, D-4
- (c) A-3, B-4, C-1, D-2
- (b) A-2, B-3, C-4, D-1

Purification of zinc

Purification of nickel

Purification of titanium

(d) A-4, B-1, C-2, D-3

List II

Ans : (c)

Match List I with List II and select the correct answer using the codes given below:

List I

- A. Cinnabar
  - 1. Zinc
- B. Cassiterite
- 2. Aluminium

List II

- C. Bauxite
- 3. Tin Mercury

D. Calamine Codes:

- (a) A 4, B 3, C 2, D 1(b) A - 1, B - 2, C - 3, D - 4
- (c) A 2, B 3, C 4, D 1
- (d) A 3, B 4, C 1, D 2

Ans : (a)

- The method of zone refining of metals is based on the principle of:
  - (a) greater mobility of the pure metal than that of impurity
  - (b) greater solubility of the impurity in the molten state than in the solid
  - (c) higher melting point of the impurity than that of the pure metal
  - (d) all above are correct

In the equation,  $4M + 8CN^- + 2H_2O + O_2 \longrightarrow$ 

 $4[M(CN)_2] + 4OH$ , the metal M is:

- (a) copper
- (b) iron

(c) gold

(d) zinc

Ans : (c)

### **OBJECTIVE QUESTIONS**



Set I: This set contains questions with one correct answer.

1.	The most abundant metal in the earth crust is:	12.	Autoreduction process is used in the extraction of:		
	[J.E.E. (W.B.) 20	10]		(a) Cu and Hg	
	(a) Al			(c) Cu and Al	
	(c) Ca		13.	In thermite process, the reducing agent is:	
2.	Which metal is generally found in native state?			(a) C	
	(a) Cu			(c) Na	
	(c) Al		14.	Complex formation method is used for the extraction of	f:
3.	A mineral is called ore if:			(a) Zn	
	(a) the metal present in the mineral is costly			(c) Hg	
	(b) a metal can be extracted from it		15.	Carbon monoxide reduction process is used for t	the
	(c) a metal can be extracted profitably from it			extraction of :	
	(d) a metal cannot be extracted from it			(a) Cu	
4.	Select the correct statement.			(c) Fe	
	(a) Dolomite is the ore of zinc		16.	Gold is extracted by hydrometallurgical process based	
	(b) Galena is the ore of mercury			its property: [C.E.T. (Karnataka) 200	05]
	(c) Pyrolusite is the ore of iron			(a) of being electropositive	. 🗆
	(d) Cassiterite is the ore of tin			(b) to form complexes which are water soluble	
5.	Which of the following pairs consists of minerals of	the		(c) of being less reactive	
	same metal?		107	(d) to form salts which are water soluble	
	(a) Bauxite, Limonite   (b) Haematite, Magnetite		17.	Argentite is a mineral of:	
	(c) Galena, Cerusite			(a) Au	
6.	Froth floatation process is based on: [P.E.T. (Kerala) 20	05]	10	(c) Ag	
	(a) specific gravity of the ore particles		10.	employed to extract:	15
	(b) magnetic properties of the ore particles			(a) lead	
	(c) wetting properties of the ore particles			(c) sodium	
	(d) electrical properties of the ore particles		10	When ZnS and PbS minerals are present together, NaCN	
7.	The function of flux during the smelting of the ore is:		17.	added to separate them in froth floatation process becau	
	(a) to make the ore porous			(a) Pb(CN) <sub>2</sub> is precipitated while there is no effect on Z	
	(b) to remove gangue			(A) 1 2 (G-3)/2 to prostprimote while the to the chief of the	
	(c) to facilitate reduction			(b) ZnS forms soluble complex, Na <sub>2</sub> Zn(CN) <sub>4</sub>	
	(d) to facilitate oxidation			(c) PbS forms soluble complex, Na <sub>2</sub> Pb(CN) <sub>4</sub>	
8.	Name the metal M which is extracted on the basis	of	-	(d) both (a) and (b)	
	following reactions:			[Hint: $ZnS + 4NaCN \longrightarrow Na_2Zn(CN)_4 + Na_2S$ ]	
	$4M + 8NaCN + 2H_2O + O_2 \longrightarrow 4NaM(CN)_2 + 4NaO_2$	H	20.	2 0.7	the
	$2NaM(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2M$			method used is:	
	(a) Au or Ag			(a) carbon reduction	
	(c) Ni			(b) carbon monoxide reduction	
9.	Which of the following statements is true?			(c) aluminothermic	
	(a) All ores are minerals			(d) electrolytic reduction	
	(b) All minerals are ores		21.	Poling process is used:	
	(c) A mineral cannot be an ore			(a) for the removal of Cu <sub>2</sub> O from Cu	
	(d) An ore cannot be a mineral			(b) for the removal of Al <sub>2</sub> O <sub>3</sub> from Al	
10.	The impurities present in the mineral are called:			(c) for the removal of Fe <sub>2</sub> O <sub>3</sub> from Fe	
	[J.E.E. (Orissa) 20	010]		(d) in all the above	
	(a) flux		22.	$ACl_2 + BCl_2 \longrightarrow ACl_4 + B \downarrow$	
	(c) alloy			· (Excess)	
11.	Electrolytic reduction process is used for the extraction	of:		$BO \xrightarrow{\text{Heat}} B + 1/2 O_2$	
	(a) alkali metals			(A and B are metals.)	
	(c) aluminium		1	The ore of $B$ is :	

	(a) cinnabar (c) galena [ <b>Hint</b> : SnCl <sub>2</sub> + HgCl			36.	The furnace lining in ste (i) CaO (ii) SiO <sub>2</sub> (iii) I (a) (ii) and (iv)	el manufacture consists of :  MgO (iv) CaCO <sub>3</sub> (b) (i) and (iii)	
	HgC	$\longrightarrow$ Hg + 1/2 O <sub>2</sub> ]	ł		(c) (iii) and (iv)	☐ (d) (ii), (iii) and (iv)	
23.	Essential constituent of a	imalgam is :	Ì	37.	The furnace which gives	the highest temperature is:	:
	(a) an alkali metal	□ (b) silver			(a) blast furnace	(b) reverberatory furn	ace 🗆
	(c) mercury	☐ (d) iron			(c) electrical furnace	☐ (d) muffle furnace	
24.	Heating of pyrites in pre-	esence of air to remove su	ulphur is	38.	Which method of pur	ification is represented by	y the
	called as:	[A.F.M.	.C. 2005]		following equations?		
	(a) roasting	☐ (b) calcination			•	J.E.E. (Orissa)	2010]
	(c) smelting	(d) fluxing			523 K	1700 K	
25.	Calamine is:	•			$Ti + 2I_2 - \frac{323 \cdot 1}{2}$	$\rightarrow$ TiI <sub>4</sub> $\xrightarrow{1700 \text{ K}}$ Ti + 2I <sub>2</sub>	
	(a) ZnSO <sub>4</sub>	□ (b) ZnO			(a) Cupellation	□ (b) Poling	
	(c). ZnS	$\Box$ (d) ZnCO <sub>3</sub>			(c) Van Arkel	☐ (d) Zone refining	
26.	Radium is obtained from	n :		39.	Van Arkel method of	purification of metals in	volves
	(a) pitchblende	☐ (b) haematite			converting the metal to	——————————————————————————————————————	
	(c) monazite	☐ (d) none of these			(a) volatile stable compe		
27.	From gold amalgam, go	ld may be recovered by :			(b) volatile unstable con	npound	
	(a) addition of Zn metal				(c) non-volatile stable of	ompound	
	(b) electrolytic refining				(d) none of the above	•	
	(c) distillation			40.	Zone refining is a method	od to obtain:	
	(d) dissolving Hg in HN	$NO_3$			(a) very high temperatu		
28.	Froth floatation process				(b) ultrapure Al		
	(a) oxide ores	☐ (b) sulphide ores			(c) ultrapure metals		
	(c) chloride ores	☐ (d) all of these			(d) ultrapure oxides		
29.	Leaching is a process of			41.	MgO can be used as ref	ractory material because:	
	(a) reduction	☐ (b) concentration			(a) it is a good electrica	-	
	(c) refining	☐ (d) oxidation			(b) it has high melting		
30.	Which one of the follow				(c) it is a good conductor	<del>-</del>	
	(a) CaCO <sub>3</sub>	(b) CaO			(d) all of these		
	(c) SiO <sub>2</sub>	☐ (d) MgO		42.		r the extraction of which me	etals ?
31.	Ore dressing for iron is	•			(i) Pb (ii) Al (iii) Ag		
	(a) froth floatation proc				-	☐ (b) (i), (ii) and (iii)	
	(b) magnetic separation				(c) (ii) and (iv)	☐ (d) (iii) and (iv)	
,	(c) hand picking			43.		the one which cannot be ob	tained
	(d) all of the above					ueous solution of its salt is	
32.		iron from haematite, lim	estone is		(a) Ag	□ (b) Mg	
	added to act as:				(c) Cu	□ (d) Al	
	(a) flux	☐ (b) slag		44.		n technique is used in the ext	raction
	(c) a reducing agent	☐ (d) an oxidising age	ent 🗆		of:	1	
33.	Carnallite is a double sa				(a) highly electronegative	ve elements	
	(a) NaCl, NaNO <sub>3</sub>	$\Box$ (b) K <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub>			(b) transition metals		
	(c) KCl, MgCl <sub>2</sub>	☐ (d) NaCl, MgCl <sub>2</sub>		1	(c) metalloids		
34.	•	reactions occur during cal	lcination?		(d) highly electropositive	ve elements	
	(i) $CaCO_3 \longrightarrow$	_		45.			
	(ii) $4\text{FeS}_2 + 11\text{O}_2 \longrightarrow$				(a) CaO	☐ (b) P <sub>2</sub> O <sub>5</sub>	
	(iii) $2Al(OH)_3 \longrightarrow$				(c) SiO <sub>2</sub>	☐ (d) MgO	
	(iv) $Cu_2S + 2CuO \longrightarrow$			46.	The metal extracted from	S .	
	(a) (i) and (iii)	☐ (b) (i) and (ii)			(a) Mg	□ (b) Al	
	(c) (i) and (iv)	☐ (d) (iii) and (iv)			(c) Ca	□ (d) Ba	
35.			*****	47.		s in which a metal is obtaine	
	(a) to remove the vola				fused state is called:		
	(b) oxidation	1		1	(a) smelting	☐ (b) roasting	
	(c) reduction				(c) calcination	☐ (d) froth floatation	
	(d) to make slag						

	,		
48.	Asbestos is a silicate mineral of calcium and :		(c) I–C, II–B, III–D, IV–A
	(a) Al		(d) I–D, II–A, III–C, IV–B $\Box$
	(c) Ba	58.	Which of the following does not contain Mg?
49.	Which method of purification is represented by the		(a) Magnetite
	following equation?		(c) Asbestos   (d) Carnallite
	$Ni + 4CO \xrightarrow{70^{\circ}C} Ni(CO)_4 \xrightarrow{180^{\circ}C} Ni + 4CO$	59.	$Ag_2S + NaCN \longrightarrow [A]$
	(a) Van Arkel		$[A] + Zn \longrightarrow [B]$
	(c) Mond		[B] is a metal. Hence, [A] and [B] are:
50.	Which oil is used as frother in froth floatation process?		(a) $Na_2[Zn(CN)_4]$ , $Zn \square$ (b) $Na[Ag(CN)_2]$ , $Ag \square$
50.	(a) Mustard oil		(c) $Na_2[Ag(CN)_4]$ , $Ag \square$ (d) $Na_3[Ag(CN)_4]$ , $Ag \square$
	(c) Olive oil	60.	Which of the following metals is leached by cyanide
51.	The incorrect statement is:		process? [A.I.E.E.E. 2002]
J1.	(a) Calamine and siderite are carbonates		(a) Ag
			(c) Al
	(b) Argentite and cuprite are oxides ☐ (c) Zinc blende and iron pyrites are sulphides ☐	61.	Pyrolusite is a/an: [D.P.M.T. 2002]
	(d) Malachite and azurite are ores of copper		(a) oxide ore $\Box$ (b) sulphide ore $\Box$
52			(c) carbide ore $\Box$ (d) not an ore $\Box$
52.	In the commercial electrochemical process for aluminium	62.	Which one of the following ores is not concentrated by froth
	extraction, the electrolyte used is :  (a) Al(OH) <sub>3</sub> in NaOH solution		floatation process? [C.E.T. (Tamil Nadu) 2002]
			(a) Copper pyrites   (b) Pentlandite
	1		(c) Pyrolusite $\Box$ (d) Zinc blende $\Box$
	(c) A molten mixture of Al <sub>2</sub> O <sub>3</sub> and Na <sub>3</sub> AlF <sub>6</sub> ☐ (d) A molten mixture of Al <sub>2</sub> O <sub>3</sub> and Al(OH) <sub>3</sub> ☐	63.	The common method of extraction of metal from oxide ores
52			is: [P.E.T. (M.P.) 2002]
53.			(a) reduction with carbon
	electrolysed using platinum electrodes, the ions discharged at the electrodes are :		(b) reduction with hydrogen
			(c) reduction with aluminium
	, ,		(d) electrolytic method
		64.	Sulphide ores of metals are usually concentrated by froth
	, , , , , , , , , , , , , , , , , , ,		floatation process. Which one of the following sulphide ores
54	(d) hydroxyl and chloride   Cassiterite is an ore of:		offers an exception and is concentrated by chemical
J <del>4</del> .	(a) Mn		leaching? [C.B.S.E. 2007]
	(c) Sb		(a) Galena
55	Cryolite is: [C.P.M.T. 2000]		(c) Sphalerite $\Box$ (d) Argentite $\Box$
55,	(a) Na <sub>3</sub> AlF <sub>6</sub> and is used in the electrolysis of alumina for	65.	Among the metals Cr, Fe, Mn, Ti, Ba and Mg, the one that
	decreasing electrical conductivity		cannot be obtained by reduction of its metal oxide by
	(b) Na <sub>3</sub> AlF <sub>6</sub> and is used in the electrolysis of alumina for		aluminium is: [P.M.T. (Kerala) 2007]
	lowering the melting point of alumina		(a) $Cr$ $\Box$ (b) $Fe$ $\Box$
	(c) Na <sub>3</sub> AlF <sub>6</sub> and is used in the electrolytic purification of	-	(c) Mn
	alumina		(e) Mg □
	(d) Na <sub>3</sub> AlF <sub>6</sub> and is used in the electrolysis of alumina	66.	Native silver metal forms a water soluble complex with a
56.	The process of converting hydrated alumina into anhydrous		dilute aqueous solution of NaCN in the presence of:
50.	alumina is called : [Roorkee (S) 2000]		[I.I.T. 2008]
	(a) roasting $\Box$ (b) smelting $\Box$		(a) nitrogen $\Box$ (b) oxygen $\Box$
	(c) dressing $\Box$ (d) calcination $\Box$		(c) carbon dioxide
57.	Match List I with List II and select the correct answer using		[Hint: $4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4[NaAg(CN)_2]$
57.	codes given below in the lists: [S.C.R.A. 2001]		+ 4NaOH]
	List I List II	67.	Which of the following factors is of no significance for
	I. cyanide process A. ultrapure Ge		roasting sulphide ores to the oxides and not subjecting the
	II. floatation process B. pine oil		sulphide ores to carbon reduction directly?[A.I.E.E.E. 2008]
	III. electrolytic reduction C. extraction of Al		(a) $CO_2$ is more volatile than $CS_2$
	IV. zone refining D. extraction of Au		(b) Metal sulphides are thermodynamically more stable
	Codes:		than CS <sub>2</sub>
	(a) I–C, II–A, III–D, IV–B		(c) $CO_2$ is thermodynamically more stable than $CS_2$
	(b) I–D, II–B, III–C, IV–A		(d) Metal sulphides are less stable than the corresponding
	(0) 1 D, 11 D, 11 T, 14 T		oxides □

	[Hint: The reduction process is on the thermodynamic stability		(a) Zinc can be oxidised by CO	
	of the products and not on their volatility.]		(b) Zinc oxide can be reduced by C	
68.	Composition of azurite mineral is: [J.E.E. (W.B.) 2008]	~	(c) Both statements (a) and (b) are true	
	(a) $CuCO_3$ · $CuO$		(d) Both statements (a) and (b) are false	
	(c) $2CuCO_3 \cdot Cu(OH)_2  \Box$ (d) $CuCO_3 \cdot 2Cu(OH)_2  \Box$	74.	The ore that is concentrated by froth floatation process	s is :
69.	Which of the following metal is not manufactured by		[C.E.T. (Karnataka)	2009]
	electrolysis? [P.M.T. (Kerala) 2008]		(a) cinnabar (b) bauxite	
	(a) Na		(c) malachite	
	(c) Al	75.	Hydro-metallurgical process of extraction of metals is l	oased
	(d) Li		on: [J.E.E. (Orissa)	2009]
<i>7</i> 0.	The method not used in metallurgy to refine the impure		(a) complex formation □ (b) hydrolysis	
	metal is: [P.M.T. (Kerala) 2008]		(c) dehydration	
	(a) Mond process $\square$ (b) Van Arkel process $\square$	76.	In alumino-thermic process, aluminium is used as:	
	(c) Amalgamation process		[J.E.E. (Orissa)	2009]
	(d) Liquidation		(a) oxidising agent	
71.	Extraction of zinc from zinc blende is achieved by:	ļ	(b) reducing agent	, $\square$
	[I.I.T. 2007]		(c) dehydrating agent	
	(a) electrolytic reduction		(d) complex formation agent	
	(b) roasting followed by reduction with carbon	<i>7</i> 7.	According to Ellingham diagram, the oxidation reacti	on of
	(c) roasting followed by reduction with another metal $\Box$		carbon and carbon monoxide may be used to reduce v	vhich
	(d) roasting followed by self reduction $\Box$		one of the following oxides at the lowest temperature	es?
	[Hint: $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$ ;		[P.E.T. (Kerala)	2010]
	$ZnO + C \xrightarrow{> 1270 \text{ K}} Zn + CO$		(a) $Al_2O_3$	
72.			(c) MgO	
<i>,</i>	the reaction: [K.C.E.T. 2006]	78.	The chemical reaction that involves roasting process	
			[E.A.M.C.E.T. (Engg.)	2010]
	(a) $Mg + \frac{1}{2}O_2 \longrightarrow MgO \square$ (b) $2Ag + \frac{1}{2}O_2 \longrightarrow Ag_2O\square$	:	(a) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$	
	(c) $C + \frac{1}{2}O_2 \longrightarrow CO$ $\square$ (d) $CO + \frac{1}{2}O_2 \longrightarrow CO_2$ $\square$		(b) $2A1 + Fe_2O_3 \longrightarrow 2Fe + Al_2O_3$	
73.	Consider the following reactions at 1000°C.		(c) $2ZnS + 3O_2 \longrightarrow 2ZnO + 3SO_2$	
	(A) $Zn(s) + \frac{1}{2}O_2(g) \longrightarrow ZnO(s);  \Delta G^{\circ} = -360 \text{ kJ mol}^{-1}$		(d) FeO + SiO <sub>2</sub> $\longrightarrow$ FeSiO <sub>3</sub>	
	(B) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);  \Delta G^{\circ} = -460 \text{ kJ mol}^{-1}$			
	Choose the correct statement at 1000°C.			
	[M.E.E. (Kerala) 2006]			
Set	II: This set contains questions with two or more	corre	ct answers.	
<i>7</i> 9.	$Ca_3(PO_4)_2$ is:		(a) Cu	
	(a) Thomas slag		(c) Mg	
	(b) used in cement manufacturing	85.	Which of the following ores is/are oxide ore(s)?	
	(c) used in manufacture of phosphorus fertilizer $\Box$		(a) Cassiterite	
	(d) used as a refractory material		(c) Cryolite	
80.	· ·	86.	1	
	(a) Fe		(B.H.U.	2007]
	(c) Ni		(a) Cu	
81.	1 ,		(c) Pb	
	(a) Hall's process	87.	9	
	(c) Serpeck's process		(a) Malachite CuCO <sub>3</sub> · Cu(OH) <sub>2</sub>	
82.	1		(b) Chalcopyrite CuFeS <sub>2</sub>	
	(a) contact process		(c) Copper glance Cu <sub>2</sub> S	
0.3	(c) Ostwald's process		(d) Azurite Cu <sub>2</sub> O	□
83.	87	88.	0 1	_
	(a) concentration of ore (b) reduction of ore		(a) Fe + Al <sub>2</sub> O <sub>3</sub> $\longrightarrow$ 2Al + Fe <sub>2</sub> O <sub>3</sub>	
04	(c) purification		(b) $ZnO + C \longrightarrow Zn + CO$	
<b>ŏ4</b> .	Which of the following metals are extracted by electrolytic		(c) $\operatorname{Cr}_2\operatorname{O}_3 + 2\operatorname{Al} \longrightarrow 2\operatorname{Cr} + \operatorname{Al}_2\operatorname{O}_3$	
	reduction ?	]	(d) $2[Ag(CN)_2]^- + Zn \longrightarrow 2Ag + [Zn(CN)_4]^{2-}$	

H	uswe	rs																	
1.	(a)	2.	(b)	3.	(c)	4.	(d)	5.	(d)	6.	(c)	7.	(b)	8.	(a)	9.	(a)	10.	(b)
11.	(d)	12.	(a)	13.	(d)	14.	(b)	15.	(c)	16.	(b)	17.	(c)	18.	(c)	19.	(b)	20.	(c)
21.	(a)	22.	(a)	23.	(c)	24.	(a)	25.	(d)	26.	(a)	27.	(c)	28.	(b)	29.	(b)	30.	(c)
31.	(b)	32.	(a)	33.	(c)	34.	(a) ·	35.	(b)	36.	(b).	37.	(c)	38.	(c)	39.	(a)	40.	(c)
41.	. (d)	42.	(a)	43.	(b) ,	44.	(d)	45.	(c)	46.	(a) .	47.	(a)	48.	(b)	49.	(c)	50.	(d)
51.	(b)	52.	(c)	53.	(c)	54.	(d)	55.	(b)	56.	(d)	57.	(b)	58.	(a)	59.	(b)	60.	(a)
61.	(a)	62.	(c)	63.	(a)	64.	(d)	65.	(e)	66.	(b)	67.	(a)	68.	(c)	69.	(d).	70.	(c)
71.	(b)	72.	(c)	73.	(b).	74.	(a)	75.	(a)	76.	(b)	77.	(b)	78.	(c)	79.	(a, b, c)	80.	(a, c)
81.	(a, b, c)	82.	(a, c, d)	83.	(a, b, c)	84.	(b, c)	85.	(a,b,d)	86.	(a,b,c)	87.	(a,b,c)	88.	(b,c,d)				



### **Objective Questions for IIT ASPIRANTS**



<ol> <li>2.</li> </ol>	The ore having two metal atoms is: (a) haematite $\Box$ (b) galena $\Box$ (c) magnetite $\Box$ (d) copper pyrites $\Box$ The metal for which, its property of formation of volatile		<ul><li>(b) Calamine and azurite are carbonates</li><li>(c) Zinc blende and pyrites are sulphides</li><li>(d) Malachite and azurite are ores of copper</li><li>[Hint: Argentite is a sulphide ore]</li></ul>	
	complex is taken into account for its extraction is: (a) cobalt $\Box$ (b) nickel $\Box$ (c) vanadium $\Box$ (d) iron $\Box$ [Hint: Nickel forms Ni(CO)4 (volatile complex) with CO which decomposes to give nickel.]		Chromium is obtained by reducing purified chromite with:  (a) red hot coke □ (b) gaseous hydrogen (c) aluminium powder □ (d) carbon monoxide  Which one of the following reactions is an example	
3.	Zone refining is based on the principle of:  (a) fractional distillation □  (b) partition coefficient □  (c) fractional crystallisation □  (d) chromatographic separation □	,.	calcination process? (a) $2Ag + 2HCl + [O] = 2AgCl + H_2O$ (b) $2Zn + O_2 = 2ZnO$ (c) $2ZnS + 3O_2 = 2ZnO + 2SO_2$	
4.		8.	<ul> <li>(d) MgCO<sub>3</sub> = MgO + CO<sub>2</sub></li> <li>The most electropositive metals are obtained from their oby:</li> <li>(a) high temperature reduction with carbon</li> <li>(b) electrolysis of fused ionic salts</li> <li>(c) self reduction</li> </ul>	
5.	Among the following, the incorrect statement is:  (a) Argentite and cuprite are oxide ores		(d) thermal decomposition	
	1. (d) 2. (b) 3. (c) 4. (a) 5. (a)	6.	(c) 7. (d) 8. (b)	
	1. (d) 2. (b) 3. (c) 4. (a) 5. (a)	6.	(c) 7. (d) 8. (b)	

### Matrix Matching Questions for IIT Aspirants

1. Match the ores of List-I with their composition in List-II:

#### List-I

#### List-II

- (a) Malachite
- (p) Sulphide of copper
- (b) Azurite
- (q) Sulphide of iron
- (c) Chalcopyrites
- (r) Oxide of copper
- (d) Cuprite
- (s) Ore containing carbonate of copper
- 2. Match the ores of List-I with their composition in List-II:

#### List-I

#### List-II

- (a) Iron pyrites
- (p) FeS<sub>2</sub>
- (b) Fool's gold
- (q) Sulphide ore
- (c) Galena
- (r)  $Fe_2O_3$
- (d) Haematite
- (s) Concentrated by froth floatation process
- 3. Match the Column-I with Column-II:

#### Column-I

#### Column-II

- (a) Van Arkel method
- (p) Purification of copper
- (b) Poling
- (q) Refining of silver

- (c) Cupellation
- (d) Solvay process
- 4. Match List-II with List-II:

#### List-I

- (a) Magnesite
- (b) Dolomite
- (c) Corundum
- (d) Bauxite
- 5. Match List-I with List-II:

### List-I

- (Metal)
- (a) Iron
- (b) Lead
- (c) Copper
- (d) Chromium

- (r) Manufacture of Na<sub>2</sub>CO<sub>3</sub>
- (s) Purification of titanium

#### List-II

- (p) Ore of magnesium
- (q) Ore of aluminium
- (r) Oxide ore
- (s) Carbonate ore

#### List-II

(Procedure of extraction)

- (p) Carbon reduction method
- (q) Self reduction
- (r) Thermite process
- (s) Hydrometallurgical process

6. Match the metals of List-I with the process of refining of List-II:

#### List-I

#### List-II

(a) Ni

(p) Mond's process

(b) Ti

(q) Van Arkel method

(c) Zr

- (r) Distillation
- (d) Zn
- (s) Pyrometallurgical process
- 7. Match the metals of List-I with the biological origin of List-II:

#### List-I

#### List-II

- (a) Chromium
- (b) Iron
- (c) Zinc
- (d) Calcium
- (p) Chloroplast
- (q) Haemoglobin

(d-r)

(d-r)

(d-r)

- (r) Eyes of cats and cows
- (s) Prown
- (t) Bones

8. Match the metals of List-I with their distribution in India List-II:

#### List-I

#### List-II

- (a) Gold
- (p) Singhbhum
- (b) Copper
- (q) Kerala coast
- (c) Thorium
- (r) Kolar (Karnataka)
- (d) Calcium (Gypsum)
- (s) Khetri
- (t) Rajasthan
- Match the Column-I with Column-II:

#### [LI.T. 2008]

#### Column-I

- (a)  $PbS \longrightarrow PbO$
- (b)  $CaCO_3 \longrightarrow CaO$
- (c)  $ZnS \longrightarrow Zn$ (d)  $Cu_2S \longrightarrow Cu$
- (p) roasting.
- (q) calcination

Column-II

- (r) carbon reduction
- (s) self reduction

(b-s)

(a-s)

(a-p)

(a-p, s)

- (a-p, q, s) (b-p, q, s)

  - (b-p)

(b-p, q)

- (b-p, s)
  - - (c-q, s)
- (c-q) (c-q, r)

(c-p, q)

(c-q, s)

- (d-r) (d-q, r)
- (a-s)

(a-p)

- (b-q) (b-p, q)
- (c-q)(c-r)

(c-p, r)

(d-t)

(d-r, s)

- (a-r) (a-p)
- (b-p, s, t) (c-q)(b-q)
- (d-t)(d-p, s)
- **Assertion-Reason Type Questions**

The questions given below consist of an Assertion (A) and Reason (R). Use the following key to choose the correct answer:

- (a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are correct and (R) is not the correct explanation of (A).
- (c) If (A) is correct but (R) is incorrect.
- (d) If (A) is incorrect but (R) is correct.
- (e) If both (A) and (R) are incorrect.
- 1. (A) All minerals are ores.
  - (R) Ores are minerals from which metal can be extracted conveniently and economically.
- 2. (A) Metals of high purity are obtained by zone refining.
  - (R) Impurities are more soluble in the melt than in pure
- 3. (A) Au, Pt, Ag, etc., are found in free state.

- (R) The metals which are noble and chemically less reactive are found in free state.
- 4. (A) Roasting is a process in which the ore is heated in presence of air.
  - (R) Concentration of sulphide ore is done by calcination method.
- 5. (A) Carnallite is a mineral of magnesium.
  - (R) Sodium is extracted by electrolysis of aqueous sodium chloride solution.
- 6. (A) Ag and Au are extracted by leaching their ores with a dilute solution of NaCN is presence of oxygen.
  - (R) Gangue particles dissolve in NaCN solution.
- 7. (A) Alumina has high conductivity.
  - (R) The mixture of alumina and cryolite is used for electrolytic reduction in order to extract aluminium.
- 8. (A) Oxide ores are concentrated by froth floatation process.
  - (R) In froth floatation process, mineral oil is used.

- 1. (d)

- 3. (a)
- 4. (c)
- 5. (e)
- 6. (c)
- 7. (d)
- 8. (e)

# INTEGER ANDWER Topic Ruestions"

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- Au + CN<sup>-</sup> + H<sub>2</sub>O + O<sub>2</sub> → [Au(CN)<sub>2</sub>]<sup>-</sup> + OH<sup>-</sup>
  How many CN<sup>-</sup> ions are involved in the above balanced equation?
- 2. In the bauxite ore,  $Al_2O_3xH_2O$ , what is the value of x?
- 3. Iron is ....th most abundant element in the earth's crust.
- 4. In Goldschmidt aluminothermic process, thermite mixture contains—parts Fe<sub>2</sub>O<sub>3</sub> and 1 part aluminium.
- 5. How many different compounds are present in carnallite?

### Auswers

- 1. (8)  $4Au + 8CN^{-} + 2H_2O + O_2 \longrightarrow 4[Au(CN)_2]^{-} + 4OH^{-}$
- 2. (2) Al<sub>2</sub>O<sub>3</sub> 2H<sub>2</sub>O
- 3. (4) Iron is 4th most abundant element in the earth's crust.
- 4. (3) 3 parts Fe<sub>2</sub>O<sub>3</sub> and one part Al.
- 5. (3)  $\frac{\text{MgCl}_2}{1} \cdot \frac{\text{KCl}}{2} \cdot \frac{6\text{H}_2\text{O}}{3}$

# Revision Exercise (Chapter 1 to 4)

# 1)

345							
SIN	GLE CORRECT ANSWER TYPE			(c) Mn, Cr, V, Sc—Decre	asing	g number of oxidation stat	es 🗆
1	The number of elements having 2d electrons out of first	02		(d) $p^6$ , $d^{10}$ , $p^3$ , $d^5$ —Decre	easin	g relative stability	
1.	The number of elements having 3d-electrons out of first	92	Q	$O^{2-}$ , F, Na <sup>+</sup> , Al <sup>3+</sup> are is			
	elements in the periodic table are:	_	2.	follow the order:	ocic	dome lons, then lone i	312.03
	(a) 80			(a) $O^{2-} > F^{-} > Na^{+}$		3+	
^	(c) 76			(a) $O > F > Na$ (b) $O^2 < F < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+ < Na^+$			
2.	The element with atomic number 118(Uuo) has been of			(c) $Al^{3+} > O^{2-} > Na^{+}$	C AI		
	covered recently. Which of the following statements is	not	•	(d) $Na^+ < Al^{3+} < O^{2-}$			
	expected for this element?		10			of D is less than that o	_
	(a) It is a radioactive element		10.	The first ionisation ener	gy (	n b is less than that o	I DC
	(b) It is a solid at room temperature	<u> </u>		because :	.1	ahama than hamillion	
	(c) It's ionisation energy is lowest in group 18			(a) boron has greater nuc			
_	(d) It is more reactive than xenon			(b) In beryllium s-electr		is removed and from c	
3.	Actinides are all:			<i>p</i> -electron is removed		1.1.1.1.1.6	
	(a) man-made elements			(c) p-electron of boron is	mo	re snielded from nucleus	
	(b) have only shortlived isotopes		11	(d) both (b) and (c)	4114-	C	
	(c) the elements from atomic number 90 to atomic num		11.	The values of electronega	_		
	103 and show variable oxidation states			4.0 respectively. The perc	_	· .	5 1S :
	(d) the elements from atomic number 90 onwards and u			(a) 90		(b) 75.5	
	the last element with atomic number 118	. 🗆	10	(c) 50.0	□ 25 Å	(d) 79.5	:
4.	An element has the configuration,		12.	Bond length of HCl is 1.2			
	$1s^2, 2s^22p^6, 3s^23p^63d^5, 4s^2$			(a) 100% ionic		( , , , , , , , , , , , , , , , , , , ,	
	to which block and group of the long form of periodic ta	ble,	10	(c) 83.18% covalent		(d) 50% covalent	
	does this belong?		15.	Which of following does		-	ture:
	(a) $d$ -block, 7th group $\square$ (b) $d$ -block, 5th group			(a) $SO_2Cl_2$		(b) $SiO_4^{2-}$	
	(c) s-block, 2nd group $\Box$ (d) p-block, 15th group	Image: control of the		(c) $SO_4^{2-}$		(d) SF <sub>4</sub>	
5.	Which one of the following statements is wrong?		14.	A molecule which posse	esses	both $sp^3$ and $sp^3d^2$ hyb	bridi-
	(a) Bromine is liquid at room temperature			sation is:			٠
	(b) Carbon has highest melting point amongst non-meta-	als		(a) $PCl_5(g)$		(b) PCl <sub>5</sub> (s)	
				(c) PCl <sub>6</sub>		(d) none of these	
	(c) Fluorine has the highest electron gain enthalpy		15.	The species which does	not :	show paramagnetism?	
	(d) Osmium possesses highest density			(a) $O_2$		(b) O <sub>2</sub> <sup>+</sup>	
6.	The number of elements in each period is:			(c) $O_2^{2-}$		(d) $H_2^+$	
	(a) twice the principal quantum number which is being fi	lled	16.	The bond angles of NH <sub>3</sub>		- · · · · · · · · · · · · · · · · · · ·	er
			10,	(a) $NH_2^- > NH_3 > NH_4^+$			<b>□</b>
	(b) twice the number of atomic orbitals available in	the		(c) $NH_3 > NH_2^- > NH_4^+$		(d) $NH_3 > NH_4^+ > NH_2^-$	
	energy level being filled		17.	Iso-structural pair among			_
	(c) twice the number of atomic mass of the elements		-,,	(a) $XeF_2$ , $IF_2$		(b) NH <sub>3</sub> , BF <sub>3</sub>	
	(d) none of the above			(c) $CO_3^{2-}$ , $SO_3^{2-}$		(d) PCl <sub>5</sub> , ICl <sub>5</sub>	
7.	The 4d-transition series contains elements having ato	mic .	10				
	numbers from :		18.	Among KO <sub>2</sub> , AlO <sub>2</sub> , BaO	2, NO	J <sub>2</sub> unpaired electron is pr	resent
	(a) 40 to 49			in:		4) VO 1 410= 1	
_	(c) 39 to 49			(a) NO <sub>2</sub> and BaO <sub>2</sub>		(b) KO <sub>2</sub> and AlO <sub>2</sub>	
8.	Which is not arranged in the correct sequence?		10	(c) KO <sub>2</sub> only		(d) BaO <sub>2</sub> only	
	(a) $d^5$ , $d^4$ , $d^2$ , $d^1$ —Increasing magnetic moments		19.	The correct hybridisation	z stai	te of sulphur atom in SF <sub>2</sub>	, SF <sub>4</sub>

(b) MO,  $M_2O_3$ ,  $MO_2$ ,  $M_2O_5$ —Increasing acidic strength  $\square$ 

and SF<sub>6</sub> molecules is respectively: (a)  $sp^3d$ ,  $sp^3$ ,  $sp^3d^2$   $\Box$  (b)  $sp^3$ ,  $sp^3d$ ,  $sp^3d^2$ (c)  $sp^3d^2$ ,  $sp^3$ ,  $sp^3d$   $\Box$  (d)  $sp^3d^2$ ,  $sp^3d$ ,  $sp^3$ 

20.	The correct order of lattice energies of the following ionic		(C) Thermite process	(3) Extraction and	
	compounds is:			purification of Ni	
	(a) NaCl $>$ MgCl <sub>2</sub> $>$ CaO $>$ Al <sub>2</sub> O <sub>3</sub>		(D) Mond's process	(4) Extraction of Cr	,
	(b) NaCl $>$ CaO $>$ MgCl <sub>2</sub> $>$ Al <sub>2</sub> O <sub>3</sub>		(a) $A = 2$ , $B = 1$ , $C = 4$ , $D =$	•	
	(c) $Al_2O_3 > MgCl_2 > CaO > NaCl$		(b) $A = 1$ , $B = 2$ , $C = 3$ , $D =$	*	
	(d) $Al_2O_3 > CaO > MgCl_2 > NaCl$		(c) $A = 4$ , $B = 3$ , $C = 2$ , $D =$	: 1	
21.	Which of the following can act both as a Bronsted acid and		(d) $A = 3$ , $B = 4$ , $C = 1$ , $D =$	: 2	
	a Bronsted base?	30	. The metal obtained by self	reduction process is:	
	(a) $NH_4^+$ $\Box$ (b) $CO_3^{2-}$ $\Box$		(a) Cu	I (b) Hg	. 🗆
	(c) $H_2SO_4$ $\square$ (d) $HS^ \square$		(c) Pb	d) All of these	
22.	Among $Al_2O_3$ , $SiO_2$ , $P_2O_3$ and $SO_2$ , the correct order of acid	Oi	NE OR MORE THAN O		
	strength is:		ISWERS TYPE	THE COMMECT	
	(a) $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$	A	ISWLING IIFL		•
	(b) $SiO_2 < SO_2 < Al_2O_3 < P_2O_3$	31	. The electronegativity of an	element:	
	(c) $Al_2O_3 < SiO_2 < SO_2 < P_2O_3$	*	(a) is its tendency to attract t	the shared electrons in a mole	cule
	(d) $SO_2 < P_2O_3 < SiO_2 < Al_2O_3$		towards itself		
23.	The strongest Bronsted base in the following anions is:		(b) is always constant		
-	(a) $ClO^ \Box$ (b) $ClO_2^ \Box$		(c) depends on the valency	of the element	
	(c) $ClO_3^ \Box$ (d) $ClO_4^ \Box$			entage of s-character in	the
24.	The strength of the acid depends on the:		hybridised state of the	-	
	(a) number of hydrogen atoms present in the molecule $\Box$	32	. In which of the following a		rrect
	(b) density	-	for the property indicated a		
	(c) oxygen content		(a) Increasing size, Al <sup>3+</sup> < 1		
	(d) concentration of hydrogen ions furnished by ionisation		(b) Increasing IE, B < C < N		
	(a) contains or all a regen to a contains or		(c) Increasing EA, I < Br <		
25	The reverse process of neutralisation is:		(d) Increasing metallic radio		
	(a) decomposition □ (b) hydrolysis □	33	. Which of the following spe		
	(c) dehydration	))	bond order?		anne
26	The conjugate base of [Al(H <sub>2</sub> O) <sub>3</sub> (OH) <sub>3</sub> ] is:		(i) $CO_2$ (ii) $N_3^-$ (iii) $O_3$	(iv) NO <sub>2</sub>	
20.	(a) $[Al(H_2O)_3(OH)_2]^+$	•			
	(c) $[Al(H_2O)_3(OH)_2]$ $\Box$ (d) $[Al(H_2O)_3(OH)_2O]$ $\Box$				
27	Which of the following processes involves roasting?	24		(d) (ii) and (iv)	
21.	~ <u>~ ~</u>	34	. Diamagnetic species are :		
	(a) $ZnCO_3 \longrightarrow ZnO + CO_2$			$\supset$ (b) $N_2^{2-}$	
	(b) $Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$		(c) O <sub>2</sub>		
	(c) $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$	- 35	. Mark the correct statement	s out of the following:	
•	(d) $Al_2O_3 \cdot 2H_2O \longrightarrow Al_2O_3 + 2H_2O$		(a) Helium has the highest	<del>-</del>	
28.	Match List-I (ores) with List-II (metals) and select the correct		(b) Chlorine has the highes		
	answer using the codes given below:		(c) Fluorine has the highes		
	List-II List-II		(d) Hg and Br are liquids a		
	(A) Bauxite (1) Al	36	. Which of the following ha		
	(B) Haematite (2) Pb		_	☐ (b) NO <sub>3</sub>	
	(C) Galena (3) Cu		, , <b>,</b>	☐ (d) H <sub>3</sub> O <sup>+</sup>	
	(D) Chalcopyrite (4) Fe	37	In the roasting process, the		
	(a) $A = 1, B = 4, C = 3, D = 2$	51	(a) below its melting point		
	(b) $A = 1, B = 4, C = 2, D = 3$		(b) for removing moisture a		
	(c) $A = 4$ , $B = 1$ , $C = 2$ , $D = 3$		- · · · ·		
	(d) $A = 4$ , $B = 1$ , $C = 3$ , $D = 2$		(c) in the presence of flux	in order to remove gangue	
29.	Match List-I with List-II and select the correct answer using	20	(d) none of the above		
	the codes given below:	38			,1
	List-II List-II		(a) oxides of Cr and Mn		
	(A) Poling (1) Refining of Ag		(b) oxides of Cr and Al	r a	
	(B) Cupellation (2) Refining of Cu		(c) Al powder and oxide of		
			(d) Al powder and oxide of	f Mn	

39. Lewis acids are :  (a) BF <sub>3</sub> □ (b) BaCl <sub>2</sub> □  (c) AlCl <sub>3</sub> □ (d) SnCl <sub>4</sub> □  40. In the reaction,	<ul> <li>50. (A) o-nitrophenol has lower boiling point than p-nitrophenol</li> <li>(R) o-nitrophenol has lower boiling point due to presence of intramolecular H-bonding while p-nitrophenol has intermolecular H-bonding.</li> </ul>
$HC_2O_4^- + PO_4^{3-} \iff HPO_4^{2-} + C_2O_4^{2-}$	MATRIX MATCHING QUESTIONS
the Bronsted bases are:	
(a) $HC_2O_4^ \Box$ (b) $PO_4^{3-}$ $\Box$	51. Match Column-I with Column-II:
(c) $HPO_4^{2-}$ $\Box$ (d) $C_2O_4^{2-}$ $\Box$	Column-II Column-II
	(a) $4s^24p^6$ (p) Metal
ASSERTION-REASON TYPE QUESTIONS	(b) $4f^{14}5d^{10}6s^2$ (q) Non-metal
The following questions consist of an Assertion (A) and	(c) $4f^15d^16s^2$ (r) Noble gas
Reason (R). Use the following key to choose the appropriate	(d) $4d^{10}5s^25p^5$ (s) Lanthanide
answer.	52. Match Column-I with Column-II:
(a) If both (A) and (R) are correct and (R) is the correct	Column-II
explanation of (A).	(a) $NH_3$ (p) $sp^3$ hybridisation
(b) If both (A) and (R) are correct but (R) is not the correct	(b) XeF <sub>6</sub> (q) One lone pair is present
explanation of (A).	(c) B <sub>2</sub> H <sub>6</sub> (r) multicentre bonds are present
(c) If (A) is correct but (R) is not correct.	(d) NH <sub>4</sub> <sup>+</sup> (s) pyramidal shape
(d) If (A) is incorrect but (R) is correct.	53. Match Column-I with Column-II:
<b>41.</b> (A) BeCl <sub>2</sub> is covalent whereas BaCl <sub>2</sub> is ionic.	Column-II Column-II
(R) Smaller is size of the cation, greater is the polarising	(a) Cyanide process (p) Extraction of Ag
power.	(b) Electrolytic reduction (q) Extraction of Au
42. (A) Mn <sup>2+</sup> is diamagnetic.	(c) Carbon reduction (r) Extraction of Al
(R) All the orbitals except $d$ -orbitals are doubly occupied.	(d) Self reduction (s) Extraction of Pb
43. (A) All F-S-F angles in SF <sub>4</sub> are greater than 90° but less than	(t) Extraction of Hg
180°.	54. Match Column-I with Column-II;
(R) The lone pair-bond pair repulsion is weaker than bond	Column-II Column-II
pair-bond pair repulsion.	(a) O <sub>2</sub> (p) Diamagnetic
44. (A) Basic nature of the following anions follows the order,	(b) N <sub>2</sub> (q) Paramagnetic
$ClO_4^- < SO_4^{2-} < Cl^- < NO_3^-$	(c) C <sub>2</sub> (r) Double bond
(R) Stronger acid has its conjugate base weaker.	(d) B <sub>2</sub> (s) Triple bond
45. (A) CaO, which is a cheap and high melting compound, is	55. Match Column-I with Column-II:

- **45.** (A) CaO, which is a cheap and high melting compound, is used in the lining of the furnace.
  - (R) CaO is used as a flux for the removal of acidic impurities like silica in the ore.
- **46.** (A) Auto reduction of ores is used for cinnabar, copper glance and galena ores.
  - (R) The sulphide ores of Hg, Cu and Pb react with their corresponding oxides to give respective metals.
- **47.** (A) Electron gain enthalpies of halogens are maximum in their respective periods.
  - (R) Fluorine has maximum value of electron gain enthalpy.
- 48. (A) Bond order can assume any value including zero.
  - (R) Lower the bond order, larger is the bond length and smaller is the bond energy.
- **49.** (A) In a change from PCl<sub>3</sub> to PCl<sub>5</sub>, the hybrid state of P remains the same.
  - (R) The shape of PCl<sub>3</sub> is pyramidal while that of PCl<sub>5</sub> is trigonal bipyramidal.

INTEGER ANSWER TYPE

Column-I

(a)  $H_3PO_2$ 

(c) H<sub>2</sub>SO<sub>4</sub>

(d)  $H_2SO_3$ 

(b) HI

56. The total number of d-block series in the periodic table are :

(p) Dibasic

(q) Monobasic

(r) Reducing agent

(s) Oxidising agent

Column-II

- 57. How many noble gases are known?
- 58. How many elements are present in third period of periodic table?
- 59. What is the electronegativity of most electronegative element on Pauling scale?
- **60.** The number of total lone pairs in  $ICl_2^-$  is:
- 61. The bond order of CO is:
- 62. How many ionisation energies can carbon have?

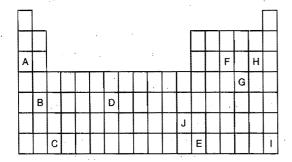
63. Lewis structure of the molecule, COCl<sub>2</sub> is O=C

What is the formal charge on carbon?

- **64.** An element has electronic configuration,  $1s^2$ ,  $2s^22p^6$  $3s^23p^63d^5$ ,  $4s^2$ . To which group of the extended form of periodic table does it belong?
- 65. In Goldschmidt-Aluminothermic process, thermite mixture contains ...... parts Fe<sub>2</sub>O<sub>3</sub> and one part Al.

#### LINKED COMPREHENSION TYPE

#### Passage 1



Analyse the table and answer the following questions:

- **66.** 'C' represents an element named:
  - (a) Yttrium
- (b) Cerium
- (c) Lanthanum
- (d) Actinium
- 67. Which of the following elements is not found in nature but has been obtained by artificial means?
  - (a) C

(c) G

- (d) J
- 68: The element which is known in gaseous state at room temperature is:
  - (a) H

(b) F

(c) G

(d) J

## Passage 2 ·

The amount of positive charge felt by the valence electrons of an atom is the effective nuclear charge. This is less than the actual nuclear charge because core electrons partially shield the valence electrons from the full positive charge of the nucleus. Shielding effect is calculated by applying Slater's rules. Atomic radii depend on the value of n of the valence shell orbitals and the effective nuclear charge experienced by the valence electrons. Atomic radii decrease from left to right in a period and from bottom to top in a group in the periodic table.

Answer the following questions:

- **69.** The atomic size of gallium is smaller than aluminium because:
  - (a) due to poor shielding effect of electrons in d-orbitals, effective nuclear charge increases in Ga

- (b) more shielding effect of d-electrons
- (c) poor shielding effect of f-orbitals in Ga
- (d) high shielding effect of 3s, 3p and 3d-electrons
- 70. The effective nuclear charge for 4s electron of Ca atom will he ·
  - (a) 17.15

(b) 20.0

(c) 2.85

- (d) 2.2
- 71. The maximum atomic radius amongst the following is for:
  - (a) Na

(b) Mg

(c) Al

(d) Si

#### Passage 3

Binary acids contain only hydrogen and another non-metal. Their strengths increase from top to bottom within a group and from left to right across a period. Oxoacids, which contain oxygen atoms in addition to hydrogen and another element, increase in strength as the number of oxygen atoms on the same central atom increases. Delocalisation of negative charge enhances the stability of the oxoacid anions, making them weaker bases and as a result, their conjugate acids are correspondingly stronger. Oxoacids having the same number of oxygen atoms generally increase in strength as the central atom moves from left to right.

Answer the following questions:

- 72. The strongest acid of the following is:
  - (a) H<sub>4</sub>SiO<sub>4</sub>
- (b)  $H_2SO_4$
- (c) HClO<sub>4</sub>
- (d) H<sub>3</sub>PO<sub>4</sub>
- 73. Which is the weakest base among the following?
  - (a) CI

(b) Br

(c) F

- 74. Consider the following compounds:

 $HO - B \qquad HO - C$ 

The electronegativities of A, B and C are in the order C > B > A. The correct order of acid strength of the above compounds is:

- (a) I < II > III
- (b) II > II > I
- (c) III < II < I
- (d) II < III < I

## Passage 4

According to valence bond theory, a covalent bond is formed between two atoms when an atomic orbital of one atom overlaps with an atomic orbital of the other and a pair of electrons with opposite spins is shared between the overlapping orbitals. In general, the better the overlap of the orbitals, the stronger the bond.

Hybrid orbitals are formed by mixing pure s, p and d orbitals. Hybrid orbitals overlap better with other orbitals than the pure atomic orbitals from which they are formed, so the bonds formed by hybrid orbitals are stronger than those formed by ordinary atomic orbitals. Two types of bonds sigma and  $\pi$ -bonds are formed by overlapping. Sigma bonds are always stronger than  $\pi$ -bonds.

#### Revision Exercise: 1 (Chapter 1 to 4)

Answer the following questions:

- 75. The orbitals of same energy level providing the most efficient overlapping are:
  - (a)  $sp^3-sp$
- (b)  $sp^2 sp^2$
- (c) *sp-sp*
- (d) all of these
- **76.** Strongest bond is formed by the head on overlapping of:
  - (a) 2s and 2s orbitals
- (b) 2p and 2p orbitals
- (c) 2s and 2p orbitals
- (d) all of these

- 77. A  $\pi$ -bond is formed by overlap of :
  - (a) s-s orbitals
  - (b) s-p orbitals
  - (c) p-p orbitals in sidewise manner
  - (d) p-p orbitals in end to end fashion

# uswers with Him

- (d) Filling of 3*d*-orbital starts from the element with atomic number 21.
- 2. (b)
- (c) These are 5f-elements from at. no. 90 to at. no. 103. Some of the members are found in nature and few of the isotopes are long-lived.
- (a) The last electron enters d-orbital, thus the element belongs to *d*-block and the group  $(3d^5 4s^2) = 5 + 2 = 7$
- 5. (c) Chlorine and not fluorine has the highest electron gain enthalpy.
- 6.
- 7. (b)
- (a) Magnetic moment depends on the number of singly occupied 8. orbitals.
- 9. (a) Ionic size decreases in isoelectronic ions when z/e ratio increases.
- (d) It is easier to remove an electron from p-orbital as it is far from nucleus than s-orbital. It is also easier to remove electron from a singly occupied orbital than a paired orbital.
- (d) % ionic character =  $16(4.0 1.0) + 3.5(4.0 1.0)^2$ = 48 + 31.5 = 79.5
- 12. (c)  $e = \frac{\mu}{d} = \frac{1.03 \times 10^{-18}}{1.275 \times 10^{-8}} = \frac{1.03}{1.275} \times 10^{-10} \text{ esu}$ % ionic character  $= \frac{100}{4.803 \times 10^{-10}} \times \frac{1.03 \times 10^{-10}}{1.275} = 16.82$ i.e., 83.18% covalent.
- 13. (d) S in SF<sub>4</sub> undergoes  $sp^3d$  hybridisation. It has a see-saw shape.
- (b)  $PCl_5(s)$  is an ionic species, *i.e.*, [PCl<sub>4</sub>]<sup>+</sup>[PCl<sub>6</sub>]<sup>-</sup>. In [PCl<sub>4</sub>]<sup>+</sup>, P undergoes sp<sup>3</sup> hybridisation while in  $[PCl_6]^-$ , P is in  $sp^3d^2$  hybridised state.
- (c)  $O_2^{2-}$  has configuration

$$KK\sigma(2s)^2 \mathring{\sigma}(2s^2) \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \mathring{\pi}(2p_x)^2 \mathring{\pi}(2p_y)^2$$

All the molecular orbitals are doubly occupied hence  $O_2^{2-}$  ion is diamagnetic.

- 16. (b) N in all the three species is in  $sp^3$  hybridised state but in NH<sub>4</sub> no lone pair is present on it but in NH3, one lone pair and in NH<sub>2</sub>, two lone pairs of electrons are present. Thus, bond angle subsequently decreases.
- 17. (a) XeF<sub>2</sub> —Linear; IF<sub>2</sub> —Linear
  - NH3-Pyramidal; BF3-Triangular planar
  - CO<sub>3</sub><sup>2</sup>—Triangular planar; SO<sub>3</sub><sup>2</sup>—Pyramidal
  - PCl5—Trigonal bipyramidal; ICl5—Square pyramidal
- 18. (c) KO<sub>2</sub> has K<sup>+</sup>O<sub>2</sub> structure. O<sub>2</sub> possesses one unpaired electron.
- (b)  $SF_2 sp^3$ ;  $SF_4 sp^3d$ ;  $SF_6 sp^3d^2$
- 20. (d)

- 22. (a)
- (a) The weakest acid furnishes strongest base anion.
- 24. (d)
- 25. (b)
- (c)  $[Al(H_2O)_3(OH)_3] \longrightarrow [Al(H_2O)_2(OH)_4]^- + H^+$ 26.
- 27.
- 28. (b)
- 29. (a)
- 30. (d)
- 31. (a, c, d)
- 32. (a, c, d)
- (a, b)  $CO_2$  and  $N_3^-$  are linear with bond order 2 in each case,  $O_3$ and NO<sub>2</sub> are V-shaped with bond order 1.5 in each case.
- 34. (a, d)
- 35. (a, b, c, d)
- 36. (a, d)
- 37. (a, b)
- 38. (c, d)
- 39. (a, c, d)
- 40. (b, d)
- 41.
- (d)  $Mn^{2+}$  is paramagnetic as its configuration is  $1s^2$ ,  $2s^22p^6$ ,
- 43. (c) The lone pair-bond pair repulsions are greater than the bond pair-bond pair repulsion, the bond angle F-S-F decreases from
- 44. (a)
- 45. (b) Both the assertion and reason are correct. CaO is used for lining of the furnace as its lattice energy is high.
- **46.** (a)
- 47. (c) Assertion is correct but reason is wrong as chlorine has maximum electron gain enthalpy.
- 48.
- (d) In change from PCl<sub>3</sub> to PCl<sub>5</sub> the hybridisation from  $sp^3$  to  $sp^3d$ 49.
- 50.
- 51. (a-q, r); (b-p); (c-p, s); (d-q)
- (a-p, q, s); (b-q); (c-p, r); (d-p)
- (a-p, q); (b-r); (c-s); (d-s, t)
- (a-q, r); (b-p, s); (c-p, r); (d-q)

55. (a-q, r); (b-q, r); (c-p, s); (d-p, r, s)

**56.** (4) 3*d*-, 4*d*-, 5*d*- and 6*d*-series.

57. (7) He, Ne, Ar, Kr, Xe, Rn and Uuo.

58. (8) Na, Mg, Al, Si, P, S, Cl, Ar.

59. (4) Fluorine is the most electronegative element.

**60.** (3) Total number of electrons in iodide ion = 8 Number of bond pairs = 2

Number of lone pairs =  $\frac{8-2}{2}$  = 3.

61. (3) CO has 14 electrons (6 + 8 = 14)M.O. configuration:

 $\sigma(1s)^2 \mathring{\sigma}(1s^2) \sigma(2s)^2 \mathring{\sigma}(2s)^2 \pi(2p_x)^2 \pi(2p_y)^2 \sigma(2p_z)^2$ 

Bond order 
$$=\frac{10-4}{2} = \frac{6}{2} = 3$$
.

**62.** (6)

**63.** (0) Formal charge on carbon =  $4 - 0 + 1/2 \times 8 = 0$ 

**64.** (7)

**65.** (3)

66. 'C' represents actinium with which 14 actinides are accommodated.

**67.** 'D' represents technetium which is not found in nature and has been obtained by artificial means.

68. (a) 'H' represents chlorine which is known in gaseous state at room temperature.

69. (a) Lesser the shielding effect more will be the force of attraction between valence electron and nucleus, smaller will be the atomic size.

**70.** (c)  $Z^* = Z - \sigma = (20 - 1 \times 0.35 + 8 \times 0.85 + 1 \times 10)$ = (20 - 17.15) = 2.85

71. (a) Shielding effect is minimum in Na amongst these elements of the same period, hence it has maximum atomic radius.

**72.** (c)

73. (d)

74. (b) Higher electronegativity will favour more acidic strength.

**75.** (c)

**76.** (b)

**77.** (c)

# Hydrogen and its Compounds

		.1 IA						17 VIIA	18 0
	<u>1</u>		IIA	 13 IIIA	14 IVA	15 VA	16 VIA		
E	2								
E	3								
1	4								
į	5								
	6								
	7								

#### Contents:

- 5.1 Position of Hydrogen in Periodic Table
- 5.2 Discovery and Occurrence
- 5.3 Preparation
- 5.4 Manufacture of Hydrogen
- 5.5 Properties of Hydrogen
- 5.5 Industrial Applications
- 5.6.1 Hydrogen Economy
- 5.7 Hydrides
- 5.8 Special Forms of Hydrogen
- 5.9 Isotopes of Hydrogen
- 5.10 Heavy Hydrogen or Deuterium
- 5.11 Tritium
- 5.12 Heavy Water or Deuterium Oxide
- 5.13 Water
- 5.14 Hard and Soft Water
- 5.15 Hydrogen Peroxide

#### Introduction

Hydrogen is the lightest element. It is most abundant element in the universe, comprising nearly 90% of all atoms and is the third most abundant element after oxygen and silicon on the surface of the earth. Most planets (stars), including our source of energy the sun, consist primarily of hydrogen. The hydrogen in the sun is the fuel for the fusion reactions that produce the life-sustaining energy which reaches our planet, *i.e.*, on the earth. The most important source of hydrogen on earth is water. The majority of hydrogen is found in oceans combined with oxygen as water.

Hydrogen atoms are the simplest of the all atoms. It is the first member of the periodic table as its atomic number is one. It has the simplest atomic structure among all the known elements. In atomic form, it consists of only one proton and a single planetary electron. Hydrogen, therefore, has the simplest electronic configuration,  $1s^1$ . The atomic form of the hydrogen exists only at very high temperatures. Normally, the elemental hydrogen is a diatomic molecule,  $H_2$  (commonly known as **dihydrogen**), the product of an exothermic reaction between H-atoms:

$$H(g) + H(g) \longrightarrow H_2(g); \Delta H^\circ = -436.4 \text{ kJ mol}^{-1}$$

The combustion of hydrogen produces more heat per gram than any other fuel. As compared to hydrocarbons, it is a "Clean fuel" because the product, water is environmentally benign. Higher consumption and least supply of hydrocarbons indicate that hydrogen gas may become the favourite fuel of the twenty-first century.

The reaction of hydrogen with oxygen to form water is an example of a reaction that requires the input of energy to get started, however, once it does, the reaction is rapid and exothermic. Because it is such an exothermic and the product is a gas, it is an ideal rocket fuel.

Hydrogen forms more compounds than any other element. These include the organic compounds, biologically important compounds and acids and bases. Hydrogen is of great industrial importance and it is said that global energy crisis can be overcome to a great extent by the use of hydrogen as a source of energy.

**Note:** Unipositive hydrogen ion (H<sup>+</sup>) i.e., proton has a very small size ( $\sim 1.5 \times 10^{-3}$  pm) compared to normal atomic and ionic sizes of 50 to 220 pm. It does not exist freely and is always associated with other atoms or molecules.



# POSITION OF HYDROGEN IN PERIODIC TABLE

There are only two elements in the first period of the periodic table, hydrogen and helium. Hydrogen is quite reactive but helium is inert. There is no difficulty in relating the structure and properties of helium with other noble gases in group 0 (or 18th), but properties of hydrogen are such that it cannot be correlated with elements of any of the main groups of the periodic table.

The configuration of hydrogen (1s<sup>1</sup>) is responsible for its dual nature, *i.e.*, either the electron can be lost behaving as electropositive element like alkali metals or the electron can be gained as to complete 1s subshell behaving as electronegative element like halogens. The position of hydrogen is not fixed in the periodic table, sometimes it is placed with alkali metals in IA group and sometimes with halogens in VIIA (or 17th) group as it resembles with alkali metals as well as with halogens. However, hydrogen exhibits other properties which differ from both alkali metals and halogens.

#### Similarities with alkali metals

On account of the following similarities of hydrogen with alkali metals, hydrogen is placed on the top of IA group.

(i) Electronic configuration: Like the alkali metals, hydrogen has only one electron in the outer shell.

Element H Li Na K Rb Cs 1; 2, 1; 2, 8, 1; 2, 8, 8, 1; 2, 8, 18, 8, 1; 2, 8, 18, 18, 18, 18, 18 Electronic 
$$1s^1$$
;  $2s^1$ ;  $3s^1$ ;  $4s^1$ ;  $5s^1$ ;  $6s^1$  configuration

(ii) Electropositive character: Like the alkali metals hydrogen has a tendency to lose its only one electron to form unipositive ion.

$$H \xrightarrow{-e} H^{+}$$

$$Li \xrightarrow{-e} Li^{+}.$$

$$Na \xrightarrow{-e} Na^{+}$$

Halides of both hydrogen and the alkali metals yield positive ions in aqueous solutions.

$$HCl \rightleftharpoons H^+ + Cl^-$$
  
 $NaCl \rightleftharpoons Na^+ + Cl^-$ 

During electrolysis, these ions are discharged at cathode. This shows that hydrogen and alkali metals both have electropositive character.

- (iii) Valency: Because of the formation of unipositive cation both hydrogen and alkali metals show electrovalency +1.
- (iv) Oxidation state: Hydrogen, like alkali metals when combines with electronegative elements shows +1 oxidation state.
- (v) Affinity for non-metals: Hydrogen as well as alkali metals have a strong affinity for nonmetals. For example, both

hydrogen and alkali metals combine with halogens to form halides, with oxygen to give oxides and with sulphur to give sulphides.

> HCl; NaCl; KCl H<sub>2</sub>O; Na<sub>2</sub>O; K<sub>2</sub>O H<sub>2</sub>S; Na<sub>2</sub>S; K<sub>2</sub>S

(vi) Reducing nature: Hydrogen, like alkali metals, acts as a reducing agent. Oxides of less reactive metals are reduced by hydrogen.

$$CuO + H_2 \longrightarrow Cu + H_2O$$
;  $CuO + 2Na \longrightarrow Cu + Na_2O$ 

#### Differences with Alkali Metals

(i) Ionisation energy: The ionisation energy of hydrogen is very high in comparison to alkali metals.

Element Hydrogen Lithium Sodium Potassium IE (kJ mol<sup>-1</sup>) 1312 520 495 418

- (ii) Nonmetallic character: Hydrogen is a nonmetal while alkali metals are metals.
- (iii) Atomicity: Hydrogen is diatomic in nature  $(H_2)$  while alkali metals are monoatomic.
- (iv) Nature of oxide: The oxide of hydrogen is neutral while oxides of alkali metals are basic in nature.
- **(v) Nature of compounds:** The compounds of hydrogen with halogens (HF, HCl, HBr, HI) are low boiling covalent compounds while halides of alkali metals are high melting ionic solids. LiF, NaCl, KBr, etc., are ionic solids.

## Similarities with Halogens

On account of the following similarities and to avoid a long gap in the first period before the second member of the period (helium), it is placed in VIIA (or 17th) group above fluorine.

- (i) Nonmetallic character: Hydrogen is a nonmetal like halogens.
- (ii) Electronic configuration: Hydrogen resembles the halogens in having one electron less than the next inert gas in its atom.

			Inert gas
1	H	1	2 He 2
9	F	2, 7	10 Ne 2, 8
17	Cl	2, 8, 7	18 Ar 2, 8, 8
35	Br	2, 8, 18, 7	36 Kr 2, 8, 18, 8

- (iii) Diatomic nature: Hydrogen forms a diatomic molecule in the elementary state similar to the halogens in which two atoms are linked together by single covalent bond (H<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>).
- (iv) Electronegative nature: Hydrogen can gain an electron and forms a negative ion like the halogens.

$$H + e \longrightarrow H^{-}; \qquad Cl + e \longrightarrow Cl^{-}$$

In the electrolysis of fused metal hydrides, hydrogen is discharged on the anode like the halogens in the electrolysis of the fused metal halides.

NaH 
$$\rightleftharpoons$$
 Na<sup>+</sup> + H<sup>-</sup> (Anode 2H<sup>-</sup>  $\longrightarrow$  H<sub>2</sub> + 2e)  
NaCl  $\rightleftharpoons$  Na<sup>+</sup> + Cl<sup>-</sup> (Anode 2Cl<sup>-</sup>  $\longrightarrow$  Cl<sub>2</sub> + 2e)

(v) Ionisation potential: The ionisation potential of hydrogen is 13.5 eV. The value is nearer to the halogens.

[Alkali metals have low values of ionisation potentials]

(vi) Similar covalent compounds and mutual replacement: Hydrogen forms several covalent compounds similar to those of halogens. For example:

$$CH_4$$
  $SiH_4$   $GeH_4$   
 $CCl_4$   $SiCl_4$   $GeCl_4$ 

Hydrogen and halogens are mutually replaceable in many covalent compounds of hydrogen and halogens.

$$CH_4 \overset{Cl}{\underset{H}{\rightleftharpoons}} CH_3Cl \overset{Cl}{\underset{H}{\rightleftharpoons}} CH_2Cl_2 \overset{Cl}{\underset{H}{\rightleftharpoons}} CHCl_3 \overset{Cl}{\underset{H}{\rightleftharpoons}} CCl_4$$

(vii) Oxidation state or number: Hydrogen, like halogens show -1 oxidation state in similar compounds.

(viii) Valency: Hydrogen, like halogens shows electrovalency as well as covalency. Hydrogen forms electrovalent compounds with strongly electropositive elements like alkali and alkaline earth metals.

Hydrogen forms covalent compounds with nonmetals.

$$\begin{array}{ccc} CH_4 & NH_3 & PH_3 \\ CCl_4 & NCl_3 & PCl_3 \end{array} \right\} \ Covalent \ compounds$$

# Differences with Halogens

- (i) Less electronegative: Hydrogen is less electronegative than halogens as it has less tendency to form H<sup>-</sup> ion. Halogens readily accept electron and form halide ions (X<sup>-</sup>).
- (ii) Nature of oxides: The oxides of halogens are acidic in nature while oxide of hydrogen is neutral.

(iii) Absence of unshared pairs of electrons: The hydrogen molecule does not have any unshared pair of electrons while in the molecules of halogens unshared pairs of electrons are present.

No doubt, hydrogen resembles alkali metals and halogens both but it is not so electropositive as alkali metals **due to high**  value of ionisation potential, similarly it is not so electronegative as halogens due to low value of electron affinity. Both the characters are equally developed in hydrogen as evident from the nature of its oxide which is neutral.

Na<sub>2</sub>O—basic (because sodium is highly electropositive)

Cl<sub>2</sub>O<sub>7</sub>—acidic (because chlorine is highly electronegative)

It is, therefore, suggested that hydrogen be alloted a separate position and not grouped with either alkali metals or halogens. Thomson assigned a separate independent position to hydrogen on the top of periodic table as shown below:

This does not disturb the symmetry of the periodic table and \_\_\_\_ there is no violation of periodic law.

In some respects, hydrogen also resembles carbon of the group IV, since both have a half filled shell of electrons.

H 1 (half of first shell maximum capacity of 2 electrons) C 2,4 (half of second shell maximum capacity of 8 electrons).

There are a number of similarities between hydrogen and organometallic compounds since the groups CH<sub>3</sub>— and H—both have one remaining valency. Thus, the hydride is often considered as part of a series of organometallic compounds, for example, LiH, LiMe, LiEt; NH<sub>3</sub>, NMe<sub>3</sub>, NEt<sub>3</sub> or SiH<sub>4</sub>, CH<sub>3</sub>SiH<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SiH<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>SiH, (CH<sub>3</sub>)<sub>4</sub>Si. Thus, hydrogen position is not fixed and hydrogen is best treated as a group on its own. Hydrogen is sometimes referred as a **'roque element'**.

# 5.2 DISCOVERY AND OCCURRENCE

Hydrogen was prepared by **Henry Cavendish** in 1766 by the action of acids on metals. It was named 'inflammable air'. **Lavoisier** named it hydrogen (hydra = water, gennas = maker) meaning water maker.

Hydrogen is the most abundant element in the universe. It occurs in nature in the free state as well as in combined state. In free state, it is present in minute quantity in air, volcanic gases and natural gas. Sun's atmosphere contains 90% of hydrogen. It is found most commonly in combination with oxygen as water. Hydrogen occurs in variety of compounds such as it occurs in mineral oils and is present in almost all the organic materials such as hydrocarbons, carbohydrates, fats, proteins, etc. Hydrogen is, thus, an essential constituent of all living things along with carbon, nitrogen and oxygen. Hydrogen is also an essential constituent of all acids and alkalies.

# 5.3 PREPARATION

There are three main sources from which hydrogen may be prepared. These are;

(i) Water (ii) Acids and (iii) Alkalies.

## (i) Hydrogen from Water

(a) Cold water reacts with alkali and alkaline earth metals to evolve hydrogen. The reactions are vigorous. To minimise the rate of reaction, alkali metals are used in the form of amalgams.

$$2Na(Hg) + 2H_2O = 2NaOH + H_2 \uparrow$$
  
Sodium amalgam

In the amalgam, only a small surface of the metal is exposed and therefore, the reaction is slow.

**(b)** Hot water or steam, when passed over hot metals like Zn, Fe, Mn, Co, Cr, Sn, etc., is decomposed to liberate hydrogen.

$$Zn + H_2O \longrightarrow ZnO + H_2\uparrow$$
  
 $3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2\uparrow$   
Red hot Steam

When steam is passed over white hot coke, hydrogen is produced in the form of water gas.

$$\begin{array}{ccc} C & + & H_2O & \longrightarrow & \underbrace{CO + H_2}_{Water\ gas} \end{array}$$

(c) By action of water on ionic hydrides: Ionic hydrides on hydrolysis with water evolve hydrogen. The hydride ion is oxidised to hydrogen. These reactions may be regarded as acid-base reactions.

$$\begin{array}{c} \text{NaH} + \text{H}_2\text{O} & \longrightarrow \text{NaOH} + \text{H}_2\\ \text{LiH} + \text{H}_2\text{O} & \longrightarrow \text{LiOH} + \text{H}_2\\ \text{CaH}_2 + 2\text{H}_2\text{O} & \longrightarrow \text{Ca(OH)}_2 + 2\text{H}_2\\ \text{(Hydrolith)} \end{array}$$

$$[H^- + H_2O \longrightarrow H_2 + OH^-]$$

Sodium borohydride also reacts with water to evolve hydrogen.

$$NaBH_4 + 2H_2O \longrightarrow NaBO_2 + 4H_2$$

(d) By the reaction of methane and steam: Both react at high temperature in presence of suitable catalyst to form hydrogen along with carbon monoxide.

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

(e) By electrolysis of water: Water is a bad conductor of electricity. Water is made a conductor either by addition of an acid or an alkali. The water containing a small amount of an acid or alkali (about 15–20%) is electrolysed in an electrolytic cell. The anode and cathode are separated by asbestos diaphragm. The cathode used is usually of iron and anode usually of nickel. The process is used at places where electric supply is cheap and easily available.

Water containing sulphuric acid: Ions present are  $H^+$ ,  $OH^-$  and  $SO_4^{2-}$ . On passing electricity  $H^+$  ions move towards cathode while  $OH^-$  and  $SO_4^{2-}$  ions move towards anode.

At cathode, hydrogen ions are discharged to give hydrogen gas.

$$2H^+ + 2e \longrightarrow 2H \longrightarrow H_2$$
  
**At anode,** OH<sup>-</sup> ions are discharged to give oxygen gas.  
OH<sup>-</sup>  $\longrightarrow$  OH + e  
 $4OH \longrightarrow 2H_2O + O_2$ 

[SO<sub>4</sub><sup>2</sup> ions are not discharged on anode as their discharge potential is higher than that of OH ions]

Water containing potassium hydroxide: Ions present are  $K^+$ ,  $OH^-$  and  $H^+$ . When current is passed,  $OH^-$  ions move towards anode while  $H^+$  and  $K^+$  ions move towards cathode.

At anode, OH ions are discharged and oxygen is evolved.

$$4OH \longrightarrow 2H_2O + O_2 + 4e$$

At cathode, H<sup>+</sup> ions are discharged and hydrogen is evolved.

$$2H^+ + 2e \longrightarrow H_2 \uparrow$$

[K<sup>+</sup> ions are not discharged as their discharge potential is higher than that of H<sup>+</sup> ions]

#### (ii) Hydrogen from Acids

(a) The metals which are reactive and occupy their position above hydrogen in the electrochemical series such as alkali metals, alkaline earth metals, Zn, Mg, Fe, etc., react with dil. HCl or dil.  $H_2SO_4$  to evolve hydrogen.

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2 \uparrow$$
  
 $Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2 \uparrow$   
 $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \uparrow$ 

 $M \to M^{2+} + 2e$  [M is electropositive and has the tendency to  $2H^+ + 2e \to H_2$  lose electrons. These electrons are accepted by protons given by dil. acids to yield hydrogen.]

(b) Mn and Mg react with dil. HNO<sub>3</sub> to evolve hydrogen.

## (iii) Hydrogen from Alkalies

Zn, Al, Sn, Pb, Si (amphoteric metals) react with boiling NaOH or KOH to evolve hydrogen.

$$Zn + 2NaOH = Na_2ZnO_2 + H_2 \uparrow$$

$$Sodium zincate$$

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2 \uparrow$$

$$Sodium meta-$$

$$aluminate$$

$$Sn + 2NaOH + H_2O = Na_2SnO_3 + 2H_2 \uparrow$$

$$Sodium stannate$$

$$Pb + 2NaOH + H_2O = Na_2PbO_3 + 2H_2 \uparrow$$

$$Sodium plumbate$$

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2 \uparrow$$

$$Sodium silicate$$

**Uyeno's method:** Very pure hydrogen is obtained with rapidity by the action of caustic potash on scrap aluminium. This method is used for military purposes.

$$2AI + 2KOH + 2H_2O = 2KAIO_2 + 3H_2 \uparrow$$

#### Laboratory Method

Hydrogen is prepared in the laboratory by the action of dilute sulphuric acid on granular (commercial) zinc in the woulfebottle. It is collected by downward displacement of air as it is lighter than air. In place of woulfe bottle, Kipp's apparatus can also be used. The apparatus should always be air tight and there should not be any flame near the apparatus otherwise explosion may occur. **Dilute H<sub>2</sub>SO<sub>4</sub> does not react with pure zinc.\*** In case of pure zinc, the addition of few drops of chloroplatinic acid or copper sulphate solution brings about the reaction.

**Purification of hydrogen gas:** Hydrogen prepared in the laboratory from granular zinc consists of a number of impurities such as AsH<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub>S, SO<sub>2</sub>, CO<sub>2</sub>, oxides of nitrogen, etc. To remove these impurities, the hydrogen is passed through three bottles containing AgNO<sub>3</sub> solution, Pb(CH<sub>3</sub>COO)<sub>2</sub> solution and KOH solution, respectively. AgNO<sub>3</sub> solution removes PH<sub>3</sub> and AsH<sub>3</sub>; Pb(CH<sub>3</sub>COO)<sub>2</sub> solution removes H<sub>2</sub>S; and the KOH solution removes CO<sub>2</sub>, SO<sub>2</sub> and oxides of nitrogen. Finally, hydrogen is collected over P<sub>2</sub>O<sub>5</sub> or anhydrous CaCl<sub>2</sub> as to remove the traces of moisture present in the hydrogen.

**Example 1.** In the laboratory, for the preparation of hydrogen from granular zinc, why the following acids cannot be used and which is the most suitable acid for this purposes:

(a) Conc.  $H_2SO_4$ 

(b) Conc. HCl

(c) Nitric acid.

**Solution:** (a) Conc. H<sub>2</sub>SO<sub>4</sub> is not used because a part of the acid gets reduced to sulphur dioxide.

$$H_2SO_4 + H_2 \longrightarrow 2H_2O + SO_2$$
(Conc.)

(b) Hydrogen liberated by the action of conc. HCl on zinc will be impure as it will contain fumes of volatile HCl. Moreover, ZnCl<sub>2</sub> formed is insoluble in conc. HCl. It will form a coating on zinc and the reaction stops after sometime.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

(c) HNO<sub>3</sub> plays a double role. It acts as an acid and as an oxidising agent. The hydrogen (nascent) first formed reduces the nitric acid into various oxides.

$$2HNO_3 + 2H \longrightarrow 2NO_2 + 2H_2O$$
  
 $2HNO_3 + 6H \longrightarrow 2NO + 4H_2O$ 

Thus, the most suitable acid is dilute H<sub>2</sub>SO<sub>4</sub>.

## Preparation of Pure Hydrogen

Pure hydrogen is obtained,

(i) by carrying electrolysis of barium hydroxide, Ba(OH)<sub>2</sub>, solution in a U-tube using platinum electrodes or nickel electrodes. The gas liberated at the cathode is passed over heated platinum gauze as to remove oxygen if present as an impurity in the form of water which is removed by passing the

gas through  $P_2O_5$ . Barium hydroxide,  $Ba(OH)_2$  is preferred to sodium hydroxide or potassium hydroxide because if any amount of  $CO_2$  is absorbed, the  $BaCO_3$  produced, being insoluble, settles down and does not interfere with electrolytic process.

(ii) by action of water on NaH,

$$NaH + H_2O \longrightarrow NaOH + H_2\uparrow$$

(iii) by Uyeno's method,

$$2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2\uparrow$$

(iv) by the action of pure dilute  $H_2SO_4$  on magnesium ribbon.

$$Mg + H_2SO_4$$
 (dil.)  $\longrightarrow MgSO_4 + H_2$ 



## MANUFACTURE OF HYDROGEN

Large quantities of hydrogen are required these days in industry for various purposes. Water is found in abundance and is the cheapest raw material from which hydrogen can be obtained. Many methods have been proposed for the commercial production of hydrogen, among which the important ones are described below:

(i) Lane's process: In this process, steam is passed over hot iron. Iron decomposes steam with the formation of magnetic oxide (Fe<sub>3</sub>O<sub>4</sub>) and hydrogen. The temperature of iron is maintained between 550 to 800°C. This reaction is termed gassing reaction and time alloted for this reaction is about 10 minutes.

3Fe + 
$$4H_2O$$
 =  $Fe_3O_4$  +  $4H_2\uparrow$  Gassing Magnetic Oxide

Iron is regenerated by reducing magnetic oxide with water gas  $(CO + H_2)$ . This reaction is called **vivifaction** and time alloted for this reaction is about 20 minutes.

$$\begin{array}{l} Fe_{3}O_{4} + 4CO = \ 3Fe + 4CO_{2} \\ Fe_{3}O_{4} + 4H_{2} = \ 3Fe + 4H_{2}O \end{array} \} \ ^{Vivifaction}$$

This iron is again used for decomposition of steam. In order to make the process continuous, the above two reactions are carried out alternatively using two or more furnaces.

(ii) Bosch's process (water-gas reactions): The considerable quantity of commercial hydrogen is obtained by the use of this method. Water gas is produced first by passing steam over hot coke at 1000°C. The temperature is not allowed to fall below 1000°C.

$$C + H_2O \longrightarrow \underbrace{CO + H_2}_{Water\ gas}$$

<sup>\*</sup>Pure zinc reacts to produce hydrogen very slowly and in small amount. The reason is that the initially formed gaseous hydrogen forms an extremely thin film on the surface of zinc which prevents the further dissolution of zinc in acid. Moreover, as a result of high over voltage established before the hydrogen can evolve from zinc surface, the discharge of H<sup>+</sup> ions or at least the combination of hydrogen atoms to form H<sub>2</sub> molecules cannot occur on pure zinc surface, so, granular zinc is preferably used. If a little CuSO<sub>4</sub> is added, a thin layer of copper is formed on zinc surface. Zinc-copper couple reacts readily with dilute acid.

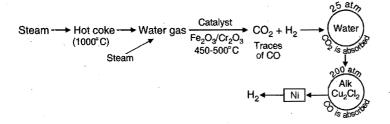
Water gas\* is mixed with twice its volume of steam and passed over a mixture of ferric oxide and chromium oxide heated to 500°C. The mixture acts as a catalyst and helps in the conversion of carbon monoxide to carbon dioxide.

$$\underbrace{H_2 + CO}_{\text{Water gas}} + \underbrace{H_2O}_{\text{Steam}} \xrightarrow{\text{Catalyst}} CO_2 + 2H_2$$

CO<sub>2</sub> dissolves in water under pressure. The mixture of CO<sub>2</sub> and H<sub>2</sub> is passed through water under a pressure of 25–30 atmospheres. CO<sub>2</sub> dissolves completely in water. Traces of CO present in hydrogen are removed by passing the gas through ammonical cuprous chloride solution under a pressure of 200 atmospheres.

The hydrogen manufactured by this method is utilised for the synthesis of ammonia in which CO acts as a poison for the catalyst. To make hydrogen completely free from CO, it is passed over nickel catalyst where any amount of CO left is converted to methane.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$



(iii) From natural gas using steam reforming process: The hydrogen on a massive industrial scale is prepared by using the steam-reforming process. This is a recent method. In this process steam and hydrocarbons from natural gas or petroleum react at high temperature and pressure in the presence of catalyst to form carbon monoxide and hydrogen. Natural gas mainly consists of methane (CH<sub>4</sub>). Hydrogen is obtained from natural gas either by partial oxidation or by cracking.

$$\begin{array}{c} \text{CH}_4 + \text{H}_2\text{O} \xrightarrow{\text{Ni-Cr}} \text{CO} + 3\text{H}_2 \\ \text{Steam} \end{array}$$

$$\begin{array}{c} \text{CO} + \text{H}_2\text{O} \xrightarrow{\text{Ni-Cr}} \text{CO}_2 + \text{H}_2 \\ \text{CH}_4 \xrightarrow{\text{Cracking}} \text{CO}_2 + \text{CO}_2$$

Natural gas is mixed with steam and passed over a catalyst at about 800-900°C. The CO<sub>2</sub> and CO are removed by the method as described in Bosch's process.

(iv) Electrolysis of water: See section 5.3 (i) (e).

(v) As a byproduct: Sodium hydroxide is manufactured by carrying electrolysis of an aqueous solution of sodium chloride in Nelson cell (Fig. 6.1) or Castner-Kellner cell (Fig. 6.2). Hydrogen and chlorine are the byproducts of this industry.

Hydrogen is also obtained as a byproduct in the manufacture of sodium by electrolysis of fused sodium hydroxide by Castner's process.

(vi) Relatively smaller quantities of hydrogen are obtained by passing a 1:1 molar mixture of vapourised methanol and water over a base metal chromite type catalyst at 400°C. The mixture of hydrogen and carbon monoxide obtained is made to react with steam to give CO<sub>2</sub> and more hydrogen.

CH<sub>3</sub>OH 
$$\xrightarrow{400^{\circ}\text{C}}$$
 CO + 2H<sub>2</sub>
CO + H<sub>2</sub>O  $\xrightarrow{400^{\circ}\text{C}}$  CO<sub>2</sub> + H<sub>2</sub>

The CO<sub>2</sub> and CO are removed by the method described in Bosch's process.

These days about 77% of the commercial hydrogen is produced from petrochemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

# 5.5 PROPERTIES OF HYDROGEN

## **Physical Properties**

- (a) It is a colourless, odourless and tasteless gas.
- (b) It is only slightly soluble in water, about 2 volumes in 100 volume of water at 0°C.
  - (c) It is lightest of all elements.

Density = 
$$0.08987 \text{ gL}^{-1}$$

(d) It is diatomic in nature.

$$C_p/C_v = \gamma = 1.40$$

(e) It has low melting and boiling points,

b.pt. = 
$$-252.5$$
°C (20.5 K)  
m.pt.=  $-259.0$ °C (14.0 K)

(f) The various physical constants are:

Ionisation potential 13.54 eV or 313 kcal mol<sup>-1</sup>
Electron affinity 17.3 kcal mol<sup>-1</sup> or 72 kJ mol<sup>-1</sup>
Electronegativity 2.1
Critical temperature -236.9°C
Bond energy, H—H 436 kJ mol<sup>-1</sup>
Bond length, H—H 74 pm

(g) Certain metals like palladium, platinum, iron, cobalt, etc., can adsorb large quantities of hydrogen. Palladium can adsorb 1000 times its own volume of hydrogen. The adsorbed hydrogen is called **occluded hydrogen** and is more active than ordinary hydrogen. This property can be used for the purification of hydrogen because only pure hydrogen is adsorbed.

<sup>\*</sup>All mixtures of CO and H<sub>2</sub> irrespective of their composition are called now-a-days synthesis gas or Syn gas. Syn gas can also be produced from sewage, sawdust, scrap wood, newspaper, etc.

#### 25 Chemical Properties

(a) Combustion: Hydrogen is inflammable or combustible gas. It burns with blue flame in oxygen atmosphere. Hydrogen, however, does not help in burning. If a burning splinter is introduced in a jar full of hydrogen, the splinter goes out while the gas burns on the mouth of the jar. On account of hydrogen burning, water is formed.

$$2H_2 + O_2 = 2H_2O$$

**(b)** Combination reactions: Hydrogen is not a very active element and does not react readily with other elements. The H—H bond dissociation enthalpy (436 kJ mol<sup>-1</sup>) is the highest for a single bond between two atoms of any element. It's dissociation is only 0.081% at 2000 K and increases to 95.5% at 5000 K.

$$H_2(g) \xrightarrow{5000 \text{ K}} 2H(g)$$

Therefore, most of the reactions of dihydrogen occur at high temperatures.

Under suitable conditions, hydrogen can be made to combine with metals and nonmetals both. (i) Alkali and alkaline earth metals (with the exception of beryllium) directly combine with hydrogen when heated in its atmosphere. The compounds formed are called hydrides.

$$2Li + H_2 = 2LiH;$$
  $Ca + H_2 = CaH_2$   
 $2Na + H_2 = 2NaH;$   $Ba + H_2 = BaH_2$ 

These hydrides are electrovalent compounds, conduct electricity in fused state. (ii) Non-metals like halogens, oxygen, sulphur, nitrogen, etc., directly combine with hydrogen under definite set of conditions and form stable covalent compounds. With fluorine, hydrogen combines readily even at low temperature while the combination with chlorine takes place in presence of sunlight or on heating. Similarly, with bromine it combines on heating while with iodine it combines when heated in presence of a catalyst.

$$H_2 + X_2 = 2HX$$
;  $X = F$ , Cl, Br or I

The reactivity of halogens towards dihydrogen decreases in the order:

$$F_2 > Cl_2 > Br_2 > I_2$$

Hydrogen combines with sulphur on ignition.

$$H_2 + S = H_2S$$

It combines with nitrogen under high pressure and in presence of a catalyst at 500°C.

$$N_2 + 3H_2 \stackrel{\text{Fe as catalyst}}{\underbrace{200 \text{ atm.}}} 2NH_3$$

It combines with carbon at about 1200°C to form methane in small amounts.

$$C + 2H_2 = CH_4$$

(c) Reducing nature: As hydrogen has great affinity for oxygen, it is suitable for removing oxygen. The oxides of less

electropositive metals such as copper, tin, iron, lead, etc., are reduced to the metals when heated in hydrogen.

$$PbO + H_2 = Pb + H_2O$$
  
 $CuO + H_2 = Cu + H_2O$   
 $Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$ 

[Note: The oxides of strongly electropositive metals such as those of alkali and alkaline earth metals are not reduced by dihydrogen.]

Numerous substances are reduced or hydrogenated by hydrogen in presence of suitable catalysts. The unsaturated fats are changed to saturated fats in the presence of finely divided nickel.

Unsaturated + 
$$H_2$$
  $\xrightarrow{\text{Ni}}$   $\xrightarrow{\text{Catalyst}}$  Saturated fat (Vanaspati ghee)

$$CH_2 = CH_2 + H_2 \xrightarrow{\text{Ni or Pt or Pd}} CH_3 - CH_3$$
Ethane

$$CH = CH + 2H_2 \xrightarrow{\text{Ni or Pt or Pd}} CH_3 - CH_3$$
Ethane

$$CH = CH + 2H_2 \xrightarrow{\text{Ni or Pt or Pd}} CH_3 - CH_3$$
Ethane

(d) Reaction with carbon monoxide: At about 700 K and under high pressure and in presence of a catalyst (ZnO/Cr<sub>2</sub>O<sub>3</sub>), dihydrogen combines with CO to form methanol.

$$CO + 2H_2 \xrightarrow{700 \text{ K}, 200 \text{ atm.}} CH_3OH$$

(e) Hydroformylation of olefins to aldehydes: Olefins combine with carbon monoxide and hydrogen in presence of octacarbonyldicobalt,  $Co_2(CO)_8$ , as catalyst under high temperature and pressure to form aldehydes which can be further reduced to alcohols.

$$\begin{array}{c} \text{R---CH} = \text{CH}_2 + \text{H}_2 + \text{CO} \longrightarrow \text{RCH}_2 - \text{CH}_2 - \text{CHO} \\ \text{Olefin} & \xrightarrow{\text{H}_2} \text{RCH}_2 - \text{CH}_2 - \text{CH}_2 \text{OH} \\ & \xrightarrow{\text{Algebral}} \end{array}$$

# 5 INDUSTRIAL APPLICATIONS

Very large quantities of hydrogen are required for synthesis of a number of products.

(a) Synthesis of ammonia: A mixture of  $N_2$  and  $H_2$  in ratio of 1:3 is compressed to 200 atmospheres and passed over heated catalyst at 500°C. About 8% NH<sub>3</sub> is formed. It is known as **Haber's process**.

$$N_2 + 3H_2 \stackrel{\text{Catalyst}}{\underbrace{\sim}} 2NH_3; \qquad \Delta H = -22.4 \text{ kcal mol}^{-1}$$

Catalyst—Freshly reduced iron having Mo as promoter.

(b) Manufacture of methyl alcohol: Water gas enriched with H<sub>2</sub> is compressed to 200 atmospheres and then passed over catalyst ZnO and CrO<sub>3</sub>, when CH<sub>3</sub>OH is formed.

$$CO + 2H_2 \xrightarrow{\text{Catalyst}} CH_3OH$$

(c) Manufacture of hydrogen chloride: Large quantities of H<sub>2</sub> and Cl<sub>2</sub> obtained as byproducts during manufacture

of NaOH are made to combine to form HCl by burning one in the other.

$$H_2 + Cl_2 \longrightarrow 2HCl$$
 (absorbed in water)

- (d) In food processing industry by hydrogenation of oils: Hydrogen is chiefly used in catalytic hydrogenation of unsaturated (liquid) oils into solid fats for the production of vegetable ghee.
- **(e) Synthetic petrol:** Petrol substitutes are obtained by subjecting a paste of powdered coal in crude oil to the action of hydrogen under pressure and in presence of a catalyst.
- (f) Oxyhydrogen flame: Oxyhydrogen flame produces a temperature of 2800°C while oxyatomic hydrogen flame produces a temperature of 4000°C. This temperature is required for melting substances having very high melting points such as quartz, platinum, etc., and also for welding purposes.
- **(g)** With helium, it is used for filling balloons employed for atmospheric study.
- **(h)** Hydrogen is used for creating a reducing atmosphere in processes like annealing and deoxidising.
- (i) As fuel for space shuttle's main rocket engine: The density of liquid hydrogen is very low (0.08987 gL<sup>-1</sup>), which is less than one-tenth that of water. This low density makes hydrogen a very light weight but bulky fuel. Hydrogen has the highest specific enthalpy of any known fuel, The low density and highest specific enthalpy of liquid hydrogen makes it a valuable fuel for space mission, so liquid hydrogen storage tank with liquid oxygen is used to power the main rocket engine of space shuttle (Fig. 5.1).

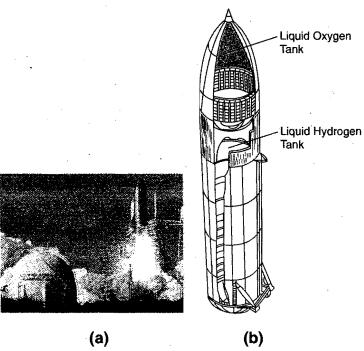


Fig. 5.1 (a) A liquid hydrogen storage tank: Liquid hydrogen is used as a rocket fuel. (b) The arrangement of fuel tanks in the space shuttle

(j) In petrochemical industry: One major use of hydrogen is in the petrochemical industry. In many cases the reaction is one where hydrogen is added to hydrocarbon compound containing carbon-carbon double bonds to produce compound that contain carbon-carbon single bond. For example, 1-butene can be reacted with hydrogen using a platinum or palladium catalyst to produce butane.

$$CH_3CH_2CH = CH_2 + H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3$$
Butane
Butane

Butane is the constituent of petrol.

# 5.6.1

#### HYDROGEN ECONOMY

(Use of hydrogen as a fuel)

The world's fossil fuel reserves are being depleted at an alarmingly fast rate. Faced with this dilemma, scientists have made intensive efforts in recent years to develop alternative sources of energy. Hydrogen has been considered as one of the alternate source of energy.

One major advantage of using hydrogen as a fuel is that it is environmentally clean, giving only water as a combustion product. If hydrogen is burned in air, small amount of nitrogen oxides can be produced because of high temperature combination of nitrogen and oxygen, but the combustion products are free from CO, CO<sub>2</sub>, SO<sub>2</sub>, unburned hydrocarbons and other environmental pollutants that result from the combustion of petroleum fuels.

The second advantage with hydrogen is that the heat of combustion of hydrogen per gram is higher than any other fuel as tabulated below:

$$H_2(g) + (\frac{1}{2})O_2(g) \longrightarrow H_2O(l)$$
;  $\Delta H^{\circ} = -284 \text{ kJ mol}^{-1}$ 

#### Energy released by combustion of some substances

Substance	Energy released (kJ/g)
Hydrogen [combustion product H <sub>2</sub> O(l)]	142
Gasoline	48
Crude petroleum	43
Typical animal fat	38.
Coal	29.3
Charcoal	29
Paper	20
Wood or dung	. 15

There has been much talk of the **hydrogen economy.** The idea is that hydrogen could replace coal and oil as major sources of energy. Our energy needs can be met by gaseous, liquid and solid hydrogen. For heating homes, gaseous hydrogen could be conveyed through underground pipes, while liquid hydrogen could be shipped by truck or rail in large vacuum insulated tanks. Automobiles might be powered by solid hydrogen in the form of solid interstitial hydrides. Prototype cars have already been built with their engines modified to run on hydrogen.

#### Hydrogen-oxygen fuel cell

There is a safer way to combine H<sub>2</sub> and O<sub>2</sub> to form water and extract energy in the form of electricity. The device is termed as a hydrogen-oxygen fuel cell (Fig. 5.2). A hydrogenoxygen fuel cell is a galvanic cell in which one of the reactants is a traditional fuel such as hydrogen. In a fuel cell, the chemical energy of a fuel is converted directly into electricity without burning the fuel. Such a cell was invented in 1839 by William Grove but it remained a mere curiosity until the advent of a U.S. programme in 1960. A fuel cell is used as a source of electrical energy in the space vehicles.It differs from an ordinary battery that the reactants are not contained within the cell but instead are continuously supplied from an external reservoir.

The fuel cell contains porous carbon electrodes impregnated with metal catalysts usually platinum and an electrolyte consisting of hot (200°C) aqueous KOH or molten Na<sub>2</sub>CO<sub>3</sub>. Proton Exchange Membrane (PEM) is used for this purpose now-a-days. The fuel (gaseous H<sub>2</sub>) and the oxidising agent (gaseous O<sub>2</sub>) do not react directly but instead flow into separate cell compartments where gaseous hydrogen is oxidised at anode and O<sub>2</sub> is reduced at the cathode. The overall cell reaction is simply the conversion of hydrogen and oxygen to water.

At the anode, hydrogen gas enters a chamber where a porous platinum catalyst oxidizes the hydrogen to  $H^{\dagger}(aq)$  ions at the anode. The hydrogen ions (H<sup>+</sup>) then migrate through a special proton exchange membrane (PEM), which works as an electrolyte and move to the cathode.

$$2H_2(g) \xrightarrow{Pt} 4H^+(aq) + 4e^- \dots$$
 (anode)

The proton exchange membrane allows a very small quantity of  $H^{+}(aq)$  ions for the passage from the anode to the cathode.

At cathode oxygen gas enters the cell, where it comes in contact with a platinum catalyst that facilitates the reduction of  $O_2(g)$  in the presence of  $H^{\dagger}(aq)$  and the electrons produced at anode from oxidation reactions and produce water.

$$O_2(g) + 4H^+(aq) + 4e^- \xrightarrow{\text{Pt}} 2H_2O(l)$$
 ...... (cathode)

Cathode

Cathode

H<sub>2</sub> gas in

Pt(catalyst)

Proton exchange membrane (PEM)

Fig. 5.2 A hydrogen-oxygen fuel cell

→ H<sub>2</sub> gas + water

vapour out

O<sub>2</sub> out ◀

Thus, there is a transfer of electrons—from  $H_2$  to  $O_2$ . The above equation is clearly the equation for the burning of hydrogen in oxygen but in this cell, it is burning without a flame and with relatively little heat. Water is the only product besides a transfer of electrons, which is what we call electricity. Hence, fuel cells are a more environmentally friendly way to produce electricity.

Fuel cells provide electricity and pure water during space flights. Fuel cells are very efficient, converting about 75% of bond energy of fuel into electricity. In contrast, an electric power plant converts 40% of bond energy of coal into electricity. However, fuel cells cannot store electrical energy. They only operate with the continuous flow of reactants. The electrode materials are short lived and expensive.

A major advantage of the fuel cell is that there is no electrode material to be replaced as there is in an ordinary battery. The fuel can be fed in continuously to produce power. In fact, hydrogen-oxygen fuel cells were used in the Gemini and-Apollo missions in the second half of the twentieth century and other space programmes.

Because of cost, large scale applications of fuel cells have been limited. The use of fuel cells is still in its infancy but will surely grow.

#### 5.7 HYDRIDES

Binary compounds of the various elements with hydrogen, in which hydrogen has usually an oxidation number of -1 are called binary hydrides. The type of hydride which an element forms depends upon its electronegativity and hence on the type of bond formed. Hydrides are conveniently studied under three classes.

- (A) Ionic or Saline or Salt like hydrides
- (B) Covalent or molecular hydrides
- (C) Metallic or interstitial hydrides

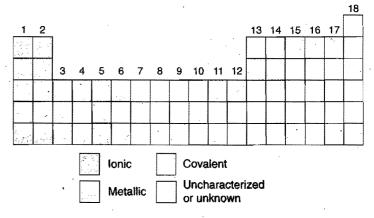


Fig. 5.3 The different classes of binary hydrogen compounds and their distribution in the periodic table

# (A) Ionic or Saline or Salt Like Hydrides

The saline hydrides are compounds of hydrogen with a strongly electropositive metals, i.e., alkali and alkaline earth metals and some highly positive members of lanthanide series with the exception of Be\* and Mg\* which can transfer electrons easily to hydrogen atoms.

These hydrides are generally prepared by heating the metal with hydrogen under pressure at temperatures between  $150^{\circ}$  to  $600^{\circ}$ C.

$$2\text{Li} + \text{H}_2 \xrightarrow{600^{\circ}\text{C}} 2\text{LiH}$$

 $H_2 + 2Na$ , K, Rb or Cs  $\xrightarrow{400^{\circ}\text{C}} 2NaH$ , 2KH, 2RbH or 2CsH

$$H_2$$
 + Ca, Sr or Ba $\xrightarrow{150-300^{\circ}C}$  Ca $H_2$ , Sr $H_2$  or Ba $H_2$ 

#### **■** Properties

(i) They are colourless or greyish coloured crystalline solids. Alkali metal hydrides have **rock-salt structure** (Fig. 5.4). They are non-conducting substances. They consist of ions and behave as salts and thereby called as **ionic hydrides**.

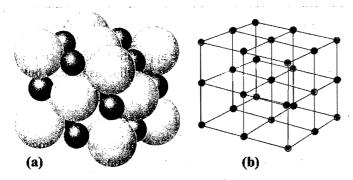


Fig. 5.4 The arrangement of ions in the rock-salt structure.

(a) The unit cell, showing the packing of the individual ions.

(b) In line diagram the red spheres are cations and the blue spheres are anions.

- (ii) They have high melting and boiling points.
- (iii) They conduct electricity in molten state (fused state) liberating hydrogen at anode. This confirms the presence of hydride (H) ions in them. For example molten LiH undergoes electrolysis.

$$LiH \xrightarrow{Li^{+}} Li^{+} + H^{-}$$
Cathode Anode
$$Li^{+} + e \longrightarrow Li \qquad 2H^{-} \longrightarrow H_{2} + 2e$$

(iv) Ionic hydrides can undergo an oxidation-reduction reaction with water to produce hydrogen and a basic solution.

$$LiH(s) + H_2O(l) \longrightarrow H_2(g) + LiOH(aq)$$

For this very reason, these hydrides can be used as a source of hydrogen gas where transportation of  $H_2(g)$  is impractical, such as for inflating weather balloons.

- (v) They have high heats of formation.
- (vi) The density of ionic hydrides is higher than those of

metals from which they are formed. This is because that H<sup>-</sup>ions occupy holes in the lattice of metal.

(vii)The stability of the hydrides decreases as the size of the cation increases.

$$LiH > NaH > KH > RbH > CsH$$
  
 $CaH_2 > SrH_2 > BaH_2$ 

Hydride	Dissociation temp. (K)	Hydride	Dissociation temp. (K)	
LiH	823	CsH	443	
NaH	483	CaH <sub>2</sub>	1158	
KH	473	SrH <sub>2</sub>	. 858	
RbH	443	$BaH_2$	503	

(viii) They burn in air on strong heating due to their decomposition into metal and hydrogen. Both readily combine with oxygen.

$$\begin{array}{cccc}
MH_2 & \longrightarrow M & + & H_2 \\
& \downarrow o_2 & & \downarrow o_2 \\
MO & & H_2O
\end{array}$$

(ix) These hydrides readily react with  $H_2O$ ,  $C_2H_5OH$ ,  $CO_2$ ,  $SO_2$ , dil. acids,  $NH_3$ , etc.

$$\begin{array}{c} \text{LiH} + \text{H}_2\text{O} \longrightarrow \text{LiOH} + \text{H}_2\uparrow\\ \text{LiH} + \text{C}_2\text{H}_5\text{OH} \longrightarrow \text{C}_2\text{H}_5\text{OLi} + \text{H}_2\uparrow\\ \text{LiH} + \text{CO}_2 \longrightarrow \text{HCOOLi}\\ \text{Lithium formate} \\ 2\text{LiH} + 2\text{SO}_2 \longrightarrow \text{Li}_2\text{S}_2\text{O}_4 + \text{H}_2\uparrow\\ \text{Lithium}\\ \text{sulphosulphite} \\ \text{LiH} + \text{NH}_3 \longrightarrow \text{LiNH}_2 + \text{H}_2\uparrow\\ \text{LiH} + \text{HCl} \longrightarrow \text{LiCl} + \text{H}_2\uparrow \end{array}$$

(x) Alkaline earth metal hydrides and LiH combine with nitrogen when heated in its atmosphere.

$$6LiH + N_2 \longrightarrow 2Li_3N + 3H_2 \uparrow$$

$$3CaH_2 + N_2 \longrightarrow Ca_3N_2 + 3H_2 \uparrow$$

(xi) Ionic hydrides show reducing properties.

$$2CO + NaH \longrightarrow HCOONa + C$$
  
 $SiCl_4 + 4NaH \longrightarrow SiH_4 + 4NaCl$   
 $PbSO_4 + 4NaH \longrightarrow PbS + 4NaOH$   
 $Fe_3O_4 + NaH \longrightarrow 3Fe + 4NaOH$ 

(xii) LiH and NaH have been used for preparing valuable reducing agents, e.g., LiAlH<sub>4</sub> (lithium aluminium hydride) and NaBH<sub>4</sub> (sodium borohydride) by the following reactions:

$$4\text{LiH} + \text{AlCl}_3 \xrightarrow{\text{Ether}} \text{LiAlH}_4 + 3\text{LiCl}$$
  
 $\text{B}_2\text{H}_6 + 2\text{NaH} \longrightarrow 2\text{NaBH}_4$ 

**Uses:** Ionic hydrides are used as reducing agents (a source of electrons during chemical reactions), as solid fuels and for ready synthesis of hydrogen via hydrolysis.

<sup>\*</sup>MgH<sub>2</sub> and BeH<sub>2</sub> show significant covalent nature.

**Note:** Binary molecular compounds of hydrogen are often called molecular hydrides, but they are not strictly hydrides as the oxidation number of hydrogen is +1 as in hydracids of halogens, oxygen, nitrogen, etc.

#### (B) Covalent or Molecular Hydrides\*

Covalent hydrides are molecular compounds in which hydrogen is covalently bonded to another element. For example some covalent hydrides are NH<sub>3</sub>, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> and HF. These hydrides are formed by all the true nonmetals (except zero group elements) and the elements like Al, Ga, Sn, Pb, Sb, Bi, Po, etc., which are normally metallic in nature, *i.e.*, this class includes the hydrides of p-block elements. Except third group elements, each other element forms a simple mononuclear hydride of the formula,  $MH_{8-x}$  where x is the number of electrons present in the outermost orbit of the element M. The simplest hydride of B and Ga are dimeric materials, B<sub>2</sub>H<sub>6</sub> (diborane) and Ga<sub>2</sub>H<sub>6</sub> respectively and the hydride of aluminium is polymeric in nature, (AlH<sub>3</sub>)<sub>n</sub>. In addition to mononuclear hydrides, the elements like Si, Ge, N, P, O, S, B, etc., form polynuclear hydrides.

Molecular hydrides are further classified according to their relative numbers of electrons and bonds in their Lewis structures.

- (i) Electron deficient molecular hydrides: These have too few electrons for writing its conventional Lewis structure. Diborane (B<sub>2</sub>H<sub>6</sub>) is an example of this type.
- (ii) Electron-precise molecular hydrides: These are formed by elements of group 14. The molecules are tetrahedral. Methane  $(CH_4)$  is an example of this type.
- (iii) Electron-rich molecular hydrides: The excess electrons are present as lone pairs. The examples are NH<sub>3</sub>, H<sub>2</sub>O, HF, etc. The hydrides NH<sub>3</sub>, H<sub>2</sub>O and HF due to the presence of highly electronegative atoms possess hydrogen bonding also.

These hydrides can be obtained by direct combination of elements or by hydrolysis of compounds such as borides, silicides, phosphides, sulphides, carbides, etc., or by use of LiAlH<sub>4</sub>.

$$N_2 + 3H_2 \longrightarrow 2NH_3$$
 $X_2 + H_2 \longrightarrow 2HX$ 
 $Mg_3B_2 + HCl(dil.) \longrightarrow A$  mixture of boron hydrides

 $Mg_2Si + HCl(dil.) \longrightarrow A$  mixture of silicon hydrides

 $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$ 
 $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$ 
 $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$ 
 $FeS + 2HCl(dil.) \longrightarrow FeCl_2 + H_2S$ 
 $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$ 
 $SiCl_4 + LiAlH_4 \xrightarrow{Ether} SiH_4 + LiCl + AlCl_3$ 
 $4BCl_3 + 3LiAlH_4 \xrightarrow{Ether} 2B_2H_6 + 3AlCl_3 + 3LiCl$ 
 $GeCl_4 + LiAlH_4 \xrightarrow{Ether} LiCl + AlCl_3 + GeH_4$ 

Some of these molecular compounds can be prepared by protonation, or proton transfer from an acid to a base, such as  $S^{2-}$ 

$$FeS(s) + 2HCl(aq) \longrightarrow FeCl_2(aq) + H_2S(g)$$

Some of these compounds can be formed from the direct reaction of the elements with hydrogen. If the nonmetal reacting with hydrogen is reactive, the reaction will readily occur without the need for elevated temperatures or a catalyst.

$$F_2(g) + H_2(g) \longrightarrow 2HF(g)$$

The reaction of hydrogen with oxygen to form water is an example of a reaction that requires the input of energy to get started. However, once it does, the reaction is rapid and exothermic.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \Delta H = -484 \text{ kJ}$$

Because it is such an exothermic reaction and the product is a gas, it is an ideal rocket fuel.

#### **■** Properties

- (i) In these hydrides, hydrogen atoms are covalently bonded to the central atom. The hydrides consist of discrete covalent molecules held together by weak van der Waals' forces and in some cases by hydrogen bonds. As a result, these hydrides are gases, liquids and in few cases solids of low melting and boiling points.
  - (ii) In general, these hydrides are volatile in nature.
  - (iii) They have low electrical conductivity.
- (iv) The thermal stability in a group decreases as the electronegativity decreases with an increase in size of the central atom. The thermal stability decreases in VA or 15th group hydrides.

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

(v) Covalent hydrides with one or more lone pairs of electrons behave as Lewis bases. Along any given period of periodic table, these hydrides become increasingly acidic as we move from left to right.

$$hinspace{:} ext{NH}_3$$
 ,  $ext{H}_2 ext{O}$  ,  $ext{HF}$  Basic Neutral Acidic

(vi) The hydrides of third group or 13th group are electron deficient and hence behave as Lewis acids.

$$B_2H_6 + 2NH_3 \longrightarrow 2[BH_3 \cdot NH_3]$$

(vii) Some hydrides act as reducing agents.

$$4AgNO_3 + SiH_4 \longrightarrow 4Ag + Si + 4HNO_3$$

(viii) The lighter elements of groups 14, 15 and 16 form polynuclear hydrides. For example, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub>, etc. for carbon; Si<sub>2</sub>H<sub>6</sub>, Si<sub>3</sub>H<sub>8</sub>, Si<sub>4</sub>H<sub>10</sub>, etc. for silicon; N<sub>2</sub>H<sub>4</sub>, N<sub>3</sub>H for nitrogen; H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>3</sub> for oxygen.

<sup>\*</sup>The systematic names of covalent or molecular hydrides are usually derived from the name of the element and suffix -ane as:  $PH_3$  Phosphane  $H_2O$  Oxidane  $NH_3$  Azane

**Uses:** Molecular hydrides have wider applications. Some of them are mentioned here. Boron hydrides are used as high energy fuels and propellants. Ammonia is the source for hydrogen at any destination. Phosphine is used for making Holme's signals. H<sub>2</sub>S is an important laboratory reagent. HF is used for etching of glass.

#### (C) Metallic or Interstitial Hydrides

Metallic hydrides are compounds containing a transition metal and hydrogen. Commonly, the formula of these compounds is  $MH_x$ , where x is often not an integer. The **metallic** hydrides are so called because they are electrically conducting.

Many transition and inner transition metals of *d*-block form black powdery, metallic or interstitial hydrides on reacting with hydrogen. However, the metals of groups 7, 8 and 9 do not form hydrides at all. Even from group 6, only chromium forms hydride (CrH). This region of periodic table from group 6 to 9 is referred to as the **hydride gap.** Metallic hydrides of groups 3, 4 and 5 are common. The elements of groups 10, 11, 12 and *f*-block elements (Ce, Eu, Yb, Th, U, etc.) on heating with H<sub>2</sub> under pressure form hydrides.

Earlier it was thought that in these compounds, hydrogen occupies **interstices** (Fig. 5.5) in the metal lattice producing distortion without any change in the metal itself. Consequently, they were termed as **interstitial hydrides**. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides have lattice different from that of the parent metal.

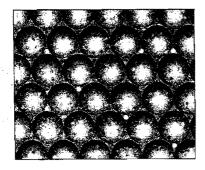


Fig. 5.5 In a metallic hydride, the small hydrogen atoms (the small grey spheres) occupy gaps-called interstices-between the larger metal atoms (the large grey spheres)

These hydrides are prepared by adsorbing hydrogen directly at appropriate temperatures by metals. In some cases, the metals are used as cathodes in the electrolysis of aqueous solutions so that hydrogen evolved at cathode is adsorbed.

The composition of these hydrides may not correspond to simple whole number ratio and therefore, they are called **non-stoichiometric hydrides.** Their composition varies with the conditions of temperature and pressure.

This shows that hydrogen atoms occupy some and not all the interstitial sites in the metallic lattice. Often hydrogen atoms enter the holes in nonstoichiometric amounts. The result is that the composition of the metallic hydride is variable. For example under one pressure of  $H_2$  the composition of the metallic  $MH_x$  might be  $MH_{0.4}$ , whereas at a higher pressure of  $H_2$ , it might be  $MH_{0.5}$ . One way to think about these compounds is to consider the metal crystal to be similar to an apartment building with the lattice holes representing the individual apartments. The occupancy of an apartment building is not fixed; it is instead a function of factors like the rent, conditions of the building and so on.

Some important examples of metallic hydrides are:  $ScH_2$ ,  $YH_2$ ,  $YH_3$ ,  $LaH_2$ ,  $LaH_3$ ,  $TiH_2$ ,  $ZrH_2$ ,  $HfH_2$ , VH,  $VH_2$ , NbH,  $NbH_2$ , TaH, CrH, etc. Some examples of non-stoichiometric hydrides are:  $PdH_{(0.6-0.8)}$ ,  $NbH_{0.11}$ ,  $ZrH_{(1.30-1.9)}$ ,  $TiH_{(1.7-2)}$ ,  $ClH_{2.7}$ ,  $La_{2.8}$ , etc.

#### Properties

- (i) They are black powdery, hard, have a metallic lustre and magnetic properties.
- (ii) They are good conductors of electricity, the conductivity, however, decreases with increase in temperature.
- (iii) The density of these hydrides is lower than those of metals from which they are formed since the crystal lattice expands due to absorption of H<sub>2</sub>.
  - (iv) They have high thermal conductivity.
- (v) They generally undergo reversible decomposition into  $H_2$  gas and metal.

$$\begin{array}{c} \text{Red hot metal} + \text{H}_2 & \xrightarrow{\text{Cool}} & \text{Interstitial} \\ & \text{hydride} \\ & & \text{Strong} \\ & \text{heating} \\ & & \text{Metal} + \text{H}_2 \\ \end{array}$$

**Uses:** (i) Metal hydrides formed as a result of occlusion can be used as hydrogen storage media.

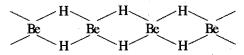
- (ii) Metallic hydrides are widely used in catalytic reduction and hydrogenation for preparing large number of useful compounds.
- (iii) Since the metallic hydrides release their hydrogen (as H<sub>2</sub>) when heated or treated with acid, they are also being investigated for storing and transporting hydrogen. Both saline and metallic hydrides have the high enthalpy densities desirable in a portable fuel.

## (d) Polymeric and Complex hydrides

Besides ionic, covalent and metallic hydrides, there are two more types of hydrides which are called as **polymeric** and **complex hydrides.** 

**Polymeric hydrides:** These are formed by elements having electronegativity in the range of 1.4 - 2.0. These are generally solids. Examples are:  $(BeH_2)_n$ ,  $(MgH_2)_n$ ,  $(AlH_3)_n$ ,  $(InH_3)_n$ ,  $(SiH_4)_n$ , etc. These hydrides consist of molecules

held together in two or three-dimensions by hydrogen bridges (Three-centre-two electron bonds.)



**Complex hydrides:** These are the compounds which contain hydride ions (H<sup>-</sup>) coordinated to metal atom. Examples are: LiAlH<sub>4</sub>, LiBH<sub>4</sub>, NaBH<sub>4</sub>, etc.

# 5.8 SPECIAL FORMS OF HYDROGEN

## (a) Nascent Hydrogen

hydrogen at the moment of formation is known as **nascent** hydrogen. It is more active than ordinary hydrogen. For example, when ordinary hydrogen is passed through acidified potassium permanganate solution or ferric chloride solution, neither of them is reduced. However, when zinc pieces are added, both get reduced.

Ordinary 
$$\longrightarrow$$
 KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub>  $\longrightarrow$  No change in colour as hydrogen

Purple coloured reduction does not occur solution

 $+$  Zn pieces

 $(Zn+dil. H_2SO_4 \rightarrow Hydrogen liberated)$ 

Decolourisation occurs, *i.e.*, liberated hydrogen reduces acidified KMnO<sub>4</sub>

It is believed that a part of energy liberated in the reaction producing hydrogen become associated with hydrogen molecules and thus make them hyper active.

# (b) Atomic Hydrogen

When hydrogen is passed through an electric arc established between two tungsten filaments, hydrogen is dissociated into atoms. This form of hydrogen is known as atomic hydrogen.

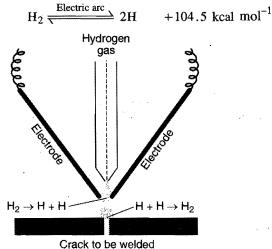


Fig. 5.6 Atomic hydrogen welding torch

The life period of atomic hydrogen is 0.3 second. It readily returns to ordinary form. This conversion is highly exothermic and used for welding purposes. This form of hydrogen is more active than ordinary hydrogen.

**Note:** (i) Atomic hydrogen can be produced at very high temperatures but nascent hydrogen is formed even at ordinary temperature.

(ii) The reducing power of atomic hydrogen is more than nascent hydrogen.

## 🤏 (c) Ortho and Para Hydrogen

Hydrogen molecule is diatomic, *i.e.*, it contains two hydrogen atoms. Each atom has one proton in the nucleus with an electron moving around it. Like electron, the proton is also spinning about an axis. Two protons in the hydrogen molecule may have either their spins in the same direction or in opposite directions giving rise to two forms **ortho** and **para**. When the proton spins are in the same direction, the form is termed as **ortho hydrogen** and when the proton spins are in the opposite directions, the form is known as **para hydrogen**.

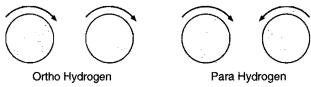


Fig. 5.7 Ortho and para hydrogen

Ordinary hydrogen is a mixture of these two forms. Ordinary hydrogen consists of 75% ortho and 25% para under ordinary atmospheric conditions. At very low temperature say about 20 K, 99.82% para and only 0.18% ortho is present but as the temperature rises, the percentage of ortho form increases while that of para form decreases reaching to a limiting ratio 75% ortho and 25% para under ordinary atmospheric conditions. This shows that intrinsic energy of ortho form is higher than para form.

The two forms differ in their physical properties like specific heat, thermal conductivity, boiling point, etc., but show similar chemical properties. Ortho form is more stable than para form. Pure para form can be obtained at low temperature (20 K) but pure ortho form is very difficult to obtain.

# 5.9 ISOTOPES OF HYDROGEN

There are three known isotopes of hydrogen, each possessing an atomic number 1 and atomic masses 1, 2 and 3 respectively, these are named as **protium**, **deuterium** and **tritium**.

- (a) The most common is the ordinary hydrogen usually called **protium** with atomic mass 1.008123. It consists of one proton in the nucleus and an electron revolving around it. This isotope constitutes 99.984 per cent of the total hydrogen available in nature. It is represented as <sup>1</sup><sub>1</sub>H.
- (b) The second isotope of hydrogen is called heavy hydrogen or deuterium. It consists of one proton and one neutron in the nucleus and an electron revolving around it. Its

atomic mass is 2.0142. It constitutes only 0.016 per cent of the total hydrogen occurring in nature. It is represented by the symbol D or <sup>2</sup>H.

(c) The third isotope of hydrogen is called **tritium.** It consists of one proton and two neutrons in the nucleus and an electron revolving around it. Its atomic mass is 3.0170. It constitutes  $1 \times 10^{-15}$  per cent of the total natural hydrogen. Unlike the above two isotopes, this isotope is unstable and shows radioactivity. It is represented by the symbol T or  ${}_{1}^{3}H$ .

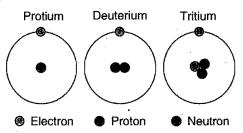


Fig. 5.8 Isotopes of hydrogen

The three isotopes have same chemical properties as they have same electronic configuration  $1s^1$ . Their physical properties are, however, different due to differences in their atomic masses. The atomic structures of three isotopes are shown in Fig. 5.8. Owing to different masses, the rates with which the three isotopes react are different. This type of difference in properties due to difference in atomic masses is called **isotopic effect.** 

Since, the percentages of deuterium and tritium present in natural hydrogen are very small, the properties of ordinarily hydrogen are mainly due to protium. Some of the important points regarding the three isotopes are tabulated below:

Property	Protium or ordinary hydrogen	Deuterium or heavy hydrogen	Tritium
Atomic number	1	1	1 .
Mass number	1 .	2	3
Exact atomic mass	1.008123	2.0142	3.0170
Symbol	iΗ	$^2_1\text{H or }^2_1\text{D}$	$^3_1$ H or $^3_1$ T
Molecular formula	$H_2$	D <sub>2</sub>	$T_2$
No. of protons in the nucleus	1	1	.1
No. of neutrons in the nucleus	Nil	1	. 2
No. of electrons	1	1	1 5
Electronic configuration	1s <sup>1</sup>	1s <sup>1</sup>	1s <sup>1</sup>
Relative abundance	99.984%	0.016%	$10^{-15}\%$
Stability (1998) 1879 (1979) (	Stable	Stable	Unstable (Radioactive)

# 5.10

#### HEAVY HYDROGEN OR DEUTERIUM

## Preparation

There are two sources from which deuterium can be obtained (i) Ordinary hydrogen, (ii) Heavy water.

## (i) Separation from ordinary hydrogen:

- (a) From liquid hydrogen: Deuterium was obtained by Urey and his co-workers by the evaporation of liquid hydrogen near its triple point 13.9 K under reduced pressure. 4 litres of liquid hydrogen are concentrated to 1 mL. The resulting liquid is found to be rich in deuterium.
- **(b) By diffusion:** Deuterium can be separated from ordinary hydrogen by the application of diffusion method. Protium being lighter diffuses more readily than deuterium. The diffusion is carried out under reduced pressure. This method is slow and tedious but produces pure deuterium.
- **(c) By adsorption on charcoal:** It is observed that protium, the lighter isotope, is adsorbed more readily and more strongly on charcoal. Thus, the ordinary hydrogen is passed over charcoal kept at liquid air temperature, most of the lighter isotope gets adsorbed and the fraction richer in deuterium passes out unchanged.

#### (ii) Preparation from heavy water

Ordinary water contains about one part of heavy water in 6000 parts of ordinary water. Heavy water is obtained from ordinary water by continuous electrolysis method in which 20 litres of water reduced to 1 mL. Now-a-days, heavy water is the important source of deuterium. The following methods can be used for the preparation of deuterium from heavy water. These methods can be even used in laboratory.

(a) By action of sodium: A pure sample of deuterium is obtained by the action of sodium on heavy water.

**(b)** By using red hot iron or tungsten: Gaseous deuterium may be prepared by decomposing heavy water with red hot iron or heated tungsten,

$$4D_2O(\text{vapours}) + 3Fe \text{ (red hot)} = Fe_3O_4 + 4D_2$$
  
 $3D_2O + W \xrightarrow{1000^{\circ}C} WO_3 + 3D_2$   
Vapours Heated electrically

The WO<sub>3</sub> formed distills over at the working temperature, exposing a fresh surface for further oxidation.

**(c) By electrolysis:** The solution of sodium carbonate (anhydrous) in heavy water on electrolysis between nickel electrodes yield deuterium on cathode.

$$2D_2O \xrightarrow{\text{Electrolysis}} 2D_2 + O_2$$

#### **Properties of Deuterium**

(a) Physical Properties: (i) It is a colourless, odourless and tasteless gas. It is insoluble in water. (ii) It is bad conductor of heat and electricity. (iii) Its density is twice that of ordinary hydrogen. The density at NTP is 0.18 g/lit.

(iv) The atomicity like ordinary hydrogen is 2 and its molecule is diatomic  $(D_2)$ . (v) The various physical constants are tabulated below:

Property	Deuterium 'D <sub>2</sub> '	'H <sub>2</sub> ' Hydrogen or protium
1 Boiling point (°C)	-249.5	-252.6
2. Melting point (°C)	-254.5	-259.1
3. Latent heat of fusion (cal/mole)	52.3	28.0
<ol> <li>Latent heat of vaporisation (cal/mole)</li> </ol>	293.0	216.0
5. Dissociation energy (kcal/mole)	104.5	102.5
6. Density at NTP (g/L)	0.18	0.09

The physical constants of deuterium are somewhat higher than protium.

- (vi) The deuterium molecule, like hydrogen, also exists in ortho and para forms. At ordinary temperature, it is a mixture of 2 parts of ortho and 1 part of para.
- **(b) Chemical Properties:** Chemically deuterium is similar to ordinary hydrogen. It enters all the reactions characteristic of the ordinary hydrogen and forms completely equivalent compounds. However, it reacts slowly and less completely than ordinary hydrogen due to heaviness.
- (i) **Burning:** Like hydrogen, it burns in air or oxygen, forming deuterium oxide,  $D_2O$  (heavy water),

$$2D_2 + O_2 \xrightarrow{560^{\circ}C} 2D_2O$$

(ii) Action with halogens: It reacts with halogens under suitable conditions to form deuterium halides which are similar to the halogen hydracids.

(iii) Combination with nitrogen: Deuterium combines with nitrogen in the presence of a catalyst to form heavy ammonia.

$$3D_2 + N_2 \xrightarrow{Catalyst} 2ND_3$$
Deutero ammonia

- (iv) Deuterium is occluded by metallic surfaces more slowly than hydrogen.
- (v) Action with unsaturated hydrocarbons: Deuterium reacts more slowly with unsaturated hydrocarbons in presence of a catalyst.

$$\begin{array}{c|c} CH_2 & CH_2D \\ \parallel & + D_2 & \xrightarrow{Ni} & \parallel \\ CH_2 & CH_2D \\ \text{Ethene} & Deutero etha \\ \end{array}$$

(vi) Action with metals: It combines with alkali and alkaline earth metals at higher temperatures. The compounds are similar to corresponding hydrides.

$$\begin{array}{ccc} 2Na + D_2 & \xrightarrow{360^{\circ}C} & 2NaD \\ & & \text{Sodium deuteride} \\ Ca + D_2 & \longrightarrow & CaD_2 \end{array}$$

(vii) Exch reactions: In a number of reactions, deuterium occupies the place of hydrogen in an ion or a molecule. The exchange reactions usually occur in presence of a catalyst like platinum black, finely divided nickel, palladium, etc.

$$\begin{array}{c} H_2O + D_2 \xrightarrow{Pt} D_2O + H_2 \\ 2NH_3 + 3D_2 \xrightarrow{Ni} 2ND_3 + 3H_2 \\ CH_4 + 2D_2 \xrightarrow{Pt} CD_4 + 2H_2 \\ Deutero \\ H_2 + D_2 \xrightarrow{600^{\circ}C} 2HD \\ Deutero hydrogen \end{array}$$

A number of compounds are known in which ordinary hydrogen has been replaced by heavy hydrogen, e.g., DNO<sub>37</sub>-D<sub>2</sub>SO<sub>4</sub>, D<sub>3</sub>PO<sub>4</sub> and also the organic compounds such as DCN, CH<sub>3</sub>COOD, C<sub>2</sub>D<sub>2</sub>, C<sub>6</sub>D<sub>6</sub>, etc., are formed.

#### Uses

- (i) It has been widely used for the preparation of deutero compounds.
- (ii) Deuterium and its compounds are used as tracers in the study of mechanism of chemical reactions and biological systems.
- (iii) One of the most important use of deuterium is as a bombarding agent in the artificial transmutation of elements.

For Example,

(iv) It is used in fusion reactions, *i.e.*, in hydrogen bombs.  ${}_{1}^{3}H + {}_{1}^{2}H \longrightarrow {}_{2}^{4}He + {}_{0}^{1}n + energy$ 

# 5.1 TRITIUM (3H or 3T)

Tritium is the isotope of hydrogen having mass 3. The existence of this isotope was confirmed by **Bleakney** and **Gould** in 1934, by spectrometric studies on samples rich in deuterium. It occurs in ordinary hydrogen in very minute quantity, *i.e.*,7 parts are present in 10<sup>7</sup> parts of ordinary hydrogen. Its oxide, T<sub>2</sub>O, is present in water in extremely minute traces and, therefore, its recovery either from ordinary hydrogen or ordinary water is not possible. Artificial transmutation reactions or nuclear reactions are used to produce tritium in very small quantities:

(a) Oliphant, Harteck and Rutherford (1934) prepared tritium by bombarding deuterium compounds with high energy deuterons.

$$_{1}^{2}H + _{1}^{2}H \longrightarrow _{1}^{3}H + _{1}^{1}H$$

(b) Tritium is produced by a number of nuclear reactions.

$${}^{9}_{4}\text{Be} + {}^{2}_{1}\text{H} \longrightarrow {}^{8}_{4}\text{Be} + {}^{3}_{1}\text{H}$$

$${}^{11}_{5}\text{B} + {}^{1}_{0}n \longrightarrow {}^{9}_{4}\text{Be} + {}^{3}_{1}\text{H}$$

$${}^{6}_{3}\text{Li} + {}^{1}_{0}n \longrightarrow {}^{4}_{2}\text{He} + {}^{3}_{1}\text{H}$$
(Slow)

This is probably the best nuclear reaction of obtaining tritium.

#### Properties

It is a gas. It boils at  $-248.1^{\circ}$ C and freezes at  $-252.4^{\circ}$ C. It is diatomic in nature. It is radioactive in nature. It undergoes a  $\beta$ -ray change. It's half life period is 12.4 years.

$${}_{1}^{3}T \longrightarrow {}_{2}^{3}He + {}_{-1}^{0}e$$

Chemically it is similar to ordinary hydrogen.

#### **Uses**

It is used in several tracer experiments. It is used in fusion reactions when large amount of energy is released.

$${}_{1}^{3}H + {}_{1}^{2}H \longrightarrow {}_{2}^{4}He + {}_{0}^{1}n + energy$$

## Physical constants of H<sub>2</sub>, D<sub>2</sub> and T<sub>2</sub>

Property	Protium (H <sub>2</sub> )	Deuterium $(D_2)$	Tritium (T <sub>2</sub> )
Boiling point (°C)	-252.6	-249.5	-248.1
Melting point (°C)	-259.1	-254.5	_252.4
Density at NTP (g/L)	0.09	0.18	0.27
Enthalpy of fusion	0.117	0.197	0.250
(kJ mol <sup>-1</sup> )			
Enthalpy of vapo-	0.904	1.226	1.393
risation (kJ mol <sup>-1</sup> )			
Enthalpy of disso-	435.88	443.35	446.9
ciation (kJ mol <sup>-1</sup> )			

Constants are in increasing order

# 5.12 HEAVY WATER OR DEUTERIUM OXIDE (D<sub>2</sub>O)

The credit for the discovery of heavy water goes to **Urey** who first proved that ordinary water contains one part of heavy water in 6000 parts of it. **Lewis** and **Donald**, in 1933, were able to isolate few millilitres of pure D<sub>2</sub>O by continuous electrolysis of water containing alkali.

#### Preparation

Heavy water is prepared by following methods:

(i) By fractional distillation of ordinary water: The boiling points of ordinary water ( $H_2O$ ) and heavy water ( $D_2O$ ) are 100°C and 101.42°C, respectively. Since, the difference in boiling points is very small, the fractional distillation of ordinary water is done in a very long fractionating column (13 metre long) and the process is repeated several times. The lighter

fraction (H<sub>2</sub>O) is distilled first while the heavier fraction (D<sub>2</sub>O) is left behind. The heavier fraction becomes richer in D<sub>2</sub>O.

- (ii) By fractional freezing: The freezing points of ordinary water and heavy water are 0°C and 3.82°C, respectively. Thus, the two materials are separated by fractional freezing. The process is repeated several times.
- (iii) Taylor, Eyring and Frost method: (Multistage electrolysis of ordinary water): Heavy water is mainly prepared by this method these days. The method is based on continuous and prolonged electrolysis of ordinary water containing NaOH.

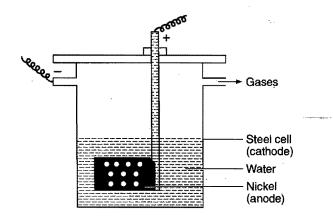


Fig. 5.9 Electrolytic cell for the preparation of heavy water

The cell used in this method is shown in Fig. 5.9. The cell dimensions are 45 cm long and 10 cm in diameter. It is made of steel. The cell itself acts as a cathode while a perforated cylindrical sheet of nickel acts as the anode. The electrolysis is completed in seven stages and in actual practice a number of electrolytic cells are used.

#### Properties of Heavy Water

**Physical Properties:** (a) Heavy water is a colourless, odourless and tasteless mobile liquid, (b) Nearly all the physical constants are higher than the corresponding values of ordinary water. The comparison of physical constants is tabulated below:

Physical Property	H <sub>2</sub> O	$D_2O$
Maximum density (g/mL)	1.00 at 277 K	1.1073 at 284.6 K
Melting point	0°C or 273 K	3.82°C or 276.82 K
Boiling point	100°C or 373K	101.42 or 374.42 K
Specific heat	1.00 cal/g K	1.01 cal/g K
Latent heat of fusion	79.7 cal/g	75.5 cal/g
Latent heat of vaporisation	539 cal/g	557 cal/g
Viscosity at 20°C	10.09 millipoise	12.6 millipoise
Surface tension at 20°C	72.8 dynes/cm	67.8 dynes/cm
Dielectric constant	78.39	78.06
Solubility of NaCl (per lit.)	359 g	305 g
Molecular mass	18.016	20.03
Dissociation constant or ionic	$1.0 \times 10^{-14}$	$0.3 \times 10^{-14}$
product at 25°C	•	,

**Chemical Properties:** Heavy water is chemically similar to ordinary water. However, D<sub>2</sub>O reacts more slowly than H<sub>2</sub>O in chemical reactions.

(a) Action with metals: D<sub>2</sub>O reacts with alkali and alkaline earth metals liberating heavy hydrogen.

$$2D_2O + 2Na \longrightarrow 2NaOD + D_2$$
Sodium
deuteroxide
$$2D_2O + Ca \longrightarrow Ca(OD)_2 + D_2$$
Calcium
deuteroxide

Vapours of heavy water are decomposed by hot metals like Zn, Fe, etc.

$$D_2O + Zn \longrightarrow ZnO + D_2$$
  
 $4D_2O + 3Fe \longrightarrow Fe_3O_4 + 4D_2$   
Magnetic  
ovide

**(b) Action with metallic oxides:** D<sub>2</sub>O reacts slowly with basic oxides to form heavy alkalies.

$$Na_2O + D_2O \longrightarrow 2NaOD$$
  
 $CaO + D_2O \longrightarrow Ca(OD)_2$ 

(c) Action with non-metallic oxides: D<sub>2</sub>O reacts slowly with acidic oxides to form deutero acids.

$$N_2O_5 + D_2O \longrightarrow 2DNO_3$$
Deutero nitric
acid

 $P_2O_5 + 3D_2O \longrightarrow 2D_3PO_4$ 
Deutero
phosphoric acid

 $SO_3 + D_2O \longrightarrow D_2SO_4$ 
Deutero
sulphuric acid

(d) Action with metallic carbides, phosphides, nitrides, arsenides, etc.: Like H<sub>2</sub>O, heavy water reacts with carbides, phosphides, nitrides, arsenides, etc., to form corresponding deutero compounds.

$$\begin{array}{c} CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2 \\ Deutero \ acctylene \end{array}$$
 
$$Al_4C_3 + 12D_2O \longrightarrow 4Al(OD)_3 + 3CD_4 \\ Deutero \ methane \end{array}$$
 
$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3 \\ Deutero \ ammonia \\ AlN + 3D_2O \longrightarrow Al(OD)_3 + ND_3 \\ Deutero \ ammonia \\ Ca_3P_2 + 6D_2O \longrightarrow 3Ca(OD)_2 + 2PD_3 \\ Deutero \ phosphine \\ Na_3As + 3D_2O \longrightarrow 3NaOD + AsD_3 \\ Deutero \ arsine \end{array}$$

(e) Electrolysis: A solution of heavy water containing Na<sub>2</sub>CO<sub>3</sub> when electrolysed evolve heavy hydrogen at cathode.

$$2D_2O \xrightarrow{\text{Electrolysis}} 2D_2 + O_2$$
(Cathode) (Anode)

**(f)** Exchange reactions: When compounds having labile hydrogen react with heavy water, hydrogen is exchanged by deuterium partially or completely.

$$NaOH + D_2O \implies NaOD + HDO$$
 $HCl(aq) + D_2O \implies DCl + HDO$ 
 $NH_4Cl(aq) + 4D_2O \implies ND_4Cl + 4HDO$ 

- (g) **Deutero-hydrates:** Heavy water like ordinary water may be associated with salts as water of crystallisation, giving deutero-hydrate, *e.g.*, Na<sub>2</sub>SO<sub>4</sub>·10D<sub>2</sub>O, CuSO<sub>4</sub>·5D<sub>2</sub>O, MgSO<sub>4</sub>·7D<sub>2</sub>O, etc.
- (h) Deuterolysis: Water brings hydrolysis of certain inorganic salts,  $D_2O$  gives similar reactions which are termed deuterolysis.

(i) Biological and physiological effects: It has been established that heavy water of high concentration retards the growth of plants and animals. It has been confirmed by Lewis that tobacco seeds do not grow in heavy water. Pure heavy water kills small fishes, tadpoles and mice, when fed on with it.

**Taylor** has shown that heavy water has germicide and bactericide properties. Water containing small quantity of  $D_2O$  acts as a tonic and stimulates vegetable growth. Certain moulds have been found to develop better in heavy water in comparison to ordinary water:

## Uses Uses

The following are the important uses of heavy water:

- (i) As a neutron moderator: Fission in uranium-235 is brought by slow speed neutrons. The substances which are used for slowing down the speed of neutrons are called moderators. Heavy water is used for this purpose in nuclear reactors.
- (ii) For the preparation of deuterium: Heavy water on electrolysis or by its decomposition with metals produces deuterium.
- (iii) As a tracer compound: Heavy water is commonly used as a tracer compound for studying various reaction mechanisms. It has also been used for studying the structure of some oxyacids of phosphorus such as H<sub>3</sub>PO<sub>2</sub> and H<sub>3</sub>PO<sub>3</sub> as to determine the number of ionisable hydrogen atoms.

**Production in India:** Various units have been set in India to manufacture heavy water. These are situated at Nangal, Trombay, Rourkela, Namrup and Neyveli.

# **5.13** WATER

Water is one of the most plentiful and readily available of all chemicals. Almost three-fourth of the earth's surface is covered with water. It is essential to life. Two-third of the human body is water. It has special importance to a chemist because of its ability to dissolve so many other substances. As a result, water serves as a medium in which a great variety of chemical reactions occur. Although it is most often perceived as a liquid at normal atmospheric pressure, water exists as a solid below 0°C and as a gas above 100°C. The terms ice and steam are used to describe the solid and gaseous states of water.

#### Properties of Pure Water

(a) Physical Properties: (i) Pure water is colourless, tasteless and odourless. It gives bluish tinge in thick layers. (ii) It freezes at 0°C and boils at 100°C. (iii) Its maximum density is 1.00 gcm<sup>-3</sup> at 4°C. (iv) It is a polar molecule and has V-shaped structure. The bond angle is 104.5°. (v) It has a high dielectric constant. The polar character of water makes it an excellent solvent for polar and ionic substances. (vi) It is a poor conductor of electricity. (vii) It has the tendency to associate. It exists in the liquid state not as a single H<sub>2</sub>O molecule but as associated molecules through hydrogen bonding [Fig. 5.11(b)]. The existence of hydrogen bonding is responsible for high values of specific heat, the latent heat of fusion and latent heat of vaporisation.

#### **Physical Constants of Water**

M.pt./K	273.0
B.pt./K	373.0
Enthalpy of formation/kJ mol <sup>-1</sup>	-285.9
Enthalpy of fusion/kJ mol-1	6.01
Enthalpy of vaporisation/kJ mol <sup>-1</sup>	40.06
Viscosity (centipoise)	0.89
Dielectric constant	78.39
Density (g cm <sup>-3</sup> )	1.00
Temp. of max. density (K)	276.98

**(b) Chemical Properties:** (i) Water is neutral in nature. pH of the pure water is 7. It is a weak electrolyte and feebly ionises into H<sup>+</sup> and OH<sup>-</sup> ions.

$$H_2O \rightleftharpoons H^+ + OH^-$$

In pure water  $[H^+] = [OH^-] = 10^{-7}$  at 25°C.

(ii) It reacts with active metals and evolves hydrogen. The reaction is exothermic in the case of alkali and alkaline earth metals.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$
  
 $Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$ 

It is decomposed by metals like Zn, Mg, Fe, etc., when steam is passed over hot metals.

$$Zn + H_2O \longrightarrow ZnO + H_2$$
  
 $3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$   
 $Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$ 

Pb and Cu decompose water only at a white heat. Ag, Au, Hg and Pt metals do not decompose water.

(iii) Reaction with nonmetals: Fluorine decomposes cold water.

$$\begin{array}{ccc} 2F_2 \,+\, 2H_2O \longrightarrow \, 2H_2F_2 \,+\, O_2 \\ \\ 3F_2 \,+\, 3H_2O \longrightarrow \, 3H_2F_2 \,+\, O_3 \end{array} \right\} Ozonised \ oxygen$$

Chlorine decomposes cold water forming HCl and HClO.

$$Cl_2 + H_2O \longrightarrow HCl + HClO$$
Hypochlorous
acid

However, in presence of sunlight only HCl is formed with liberation of oxygen.

$$2Cl_2 + 2H_2O \xrightarrow{\text{Sunlight}} 4HCl + O_2$$

When steam is passed over red hot coke (1000°C), water gas is formed.

$$C + H_2O \longrightarrow \underbrace{CO + H_2}_{\text{Water gas}}$$

(iv) Action on nonmetallic oxides: Acidic oxides combine with water to form acids.

$$CO_2 + H_2O \Longrightarrow H_2CO_3$$
 (Carbonic acid)  
 $SO_2 + H_2O \longrightarrow H_2SO_3$  (Sulphurous acid)  
 $SO_3 + H_2O \longrightarrow H_2SO_4$  (Sulphuric acid)  
 $P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$  (Orthophosphoric acid)  
 $N_2O_5 + H_2O \longrightarrow 2HNO_3$  (Nitric acid)  
 $Cl_2O_7 + H_2O \longrightarrow 2HClO_4$  (Perchloric acid)

(v) Action on metallic oxides: Basic oxides combine with water to form alkalies.

$$Na_2O + H_2O \longrightarrow 2NaOH$$
  
 $CaO + H_2O \longrightarrow Ca(OH)_2$ 

(vi) Action on hydrides, carbides, nitrides, phosphides: Water decomposes these compounds with liberation of hydrogen, acetylene (or methane), ammonia, phosphine respectively.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

(vii) Hydrolysis: Many salts specially the salts of strong bases with weak acids, weak bases with strong acids and weak bases with weak acids undergo hydrolysis with water.

$$CH_3COONa + H_2O \Longrightarrow CH_3COOH + NaOH$$
  
 $CH_3COONH_4 + H_2O \Longrightarrow CH_3COOH + NH_4OH$   
 $FeSO_4 + 2H_2O \Longrightarrow Fe(OH)_2 + H_2SO_4$ 

Some salts on hydrolysis form oxy compounds.

$$\begin{array}{c} BiCl_3 + H_2O \longrightarrow & BiOCl + 2HCl \\ & Bismuth \\ & oxychloride \\ SbCl_3 + H_2O \longrightarrow & SbOCl + 2HCl \\ & Antimony \\ & oxychloride \\ \end{array}$$

Halides of nonmetals are decomposed by water.

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$
  
 $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$   
 $SO_2Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$   
 $SiCl_4 + 3H_2O \longrightarrow H_2SiO_3 + 4HCl$ 

(viii) **Decomposition:** Water containing either alkali or acid when electrolysed gets decomposed into  $H_2$  and  $O_2$ .

$$2H_2O \longrightarrow 2H_2 + O_2$$

When heated at 2500°C, it breaks up into hydrogen and oxygen to a small extent (4%).

(ix) Water of crystallisation: It combines with many salts during crystallisation to form hydrates, e.g.,

The water present in the hydrates is called water of hydration or water of crystallisation.

The hydrates can be classified into the following three categories:

- (a) Water molecules are coordinated to the central metal ion to form complex ions. For example, in chromic chloride hexahydrate, the six molecules are linked to the central  $Cr^{3+}$  ion,  $[Cr(H_2O)_6]Cl_3$ .
- (b) Water molecules are linked to some oxygen containing anions by hydrogen bonding. For example, in  $CuSO_4 \cdot 5H_2O$ , four  $H_2O$  molecules are coordinated to the central  $Cu^{2+}$  ion while the fifth  $H_2O$  molecule is linked to  $SO_4^{2-}$  ion by hydrogen bonding.
- (c) Water molecules are present in interstitial sites or voids in the crystal lattice. For example, in barium chloride dihydrate, BaCl<sub>2</sub>·2H<sub>2</sub>O, the two water moelcules occupy the voids in the crystal lattice.
- (x) Water as a catalyst: Water acts as a catalyst in many reactions. Perfectly dry gases generally do not react but the presence of moisture brings the chemical change. Ammonia and hydrochloric acid gas combine only in presence of moisture.

#### Tests of water

- (i) A drop of water when added to anhydrous copper sulphate, changes its colour from white to blue.
- (ii) Water reacts with CaC<sub>2</sub> to evolve acetylene which burns with bright flame.

#### **Structure of Water Molecule**

Oxygen atom in water molecule is  $sp^3$  hybridized, four hybrid orbitals directed towards the corners of a tetrahedral are formed. Two of the hybrid orbitals having one electron each overlap with two hydrogen atoms and form two sigma bonds. Thus, the molecule has a bent structure with a bond angle of  $104.5^{\circ}$  (Fig. 5.10). The bond angle is less than the expected angle in tetrahedron due to the presence of two lone pairs of electrons on two uncombined hybrid orbitals which repel each other and the bonded pairs cause them to come closer and thereby reducing the bond angle from  $109^{\circ}28'$  to  $104.5^{\circ}$ . Because of high electronegativity of oxygen, the O—H bonds are polar, *i.e.*, oxygen is partially negatively charged and each hydrogen is partially positively charged. The molecule is polar and possesses dipole moment (1.84 D). Molecules are linked with each other by hydrogen bonding [Fig. 5.11 (b)].

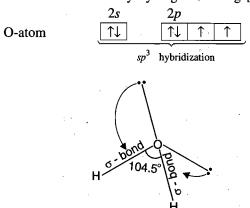


Fig. 5.10

**Example 2.** Explain, why the density of ice is less than water? or why there is decrease in volume when ice melts?

**Solution:** In ice each molecule of H<sub>2</sub>O is surrounded by three H<sub>2</sub>O molecules in hexagonal honey comb manner as shown in Fig. 5.11 (a). On the other hand in water, each molecule is surrounded by four neighbouring molecules randomly [Fig. 5.11 (b)]. This arrangement gives rise to an open-cage like structure. There are evidently, a number of 'holes' or open spaces. In such a structure lesser number of molecules are packed per mL. When ice melts a large number of hydrogen bonds are broken. The molecules, therefore, move into the holes or open spaces and come closer to each other than they were in solid state. This results sharp increase in the density. Thus, ice has lower density than water and there is contraction in volume. The contraction continues from 0°C to

4°C as the hydrogen bonds are broken progressively. The density of water is maximum at 4°C.

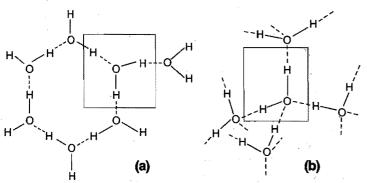


Fig. 5.11 (a) Hexagonal honey comb structure of ice. In ice each molecule of H<sub>2</sub>O is surrounded by three neighbouring H<sub>2</sub>O molecules (b) In water, each H<sub>2</sub>O molecule is surrounded by four neighbouring H<sub>2</sub>O molecules randomly

# 5.14 HARD AND SOFT WATER

A water is said to be the soft if it produces sufficient lather with the soap and water is described as being hard if it forms an insoluble scum before it forms a lather with soap\*. The hardness of natural water is generally caused by presence of the bicarbonates and sulphates of calcium and magnesium but infact all soluble salts that form a scum with soap cause hardness.

$$\operatorname{Ca}^{2+}(aq) + 2\operatorname{C}_{17}\operatorname{H}_{35}\operatorname{COO}^{-}(aq) \longrightarrow (\operatorname{C}_{17}\operatorname{H}_{35}\operatorname{COO})_2\operatorname{Ca}$$

$$\operatorname{Mg}^{2+}(aq) + 2\operatorname{C}_{17}\operatorname{H}_{35}\operatorname{COO}^{-}(aq) \longrightarrow (\operatorname{C}_{17}\operatorname{H}_{35}\operatorname{COO})_2\operatorname{Mg}$$
Anion of soap Insoluble precipitates

Soap will not produce lather with water until all the calcium and magnesium ions have been precipitated. Hard water thus wastes soap. Hardness of water is of two types:

- (a) Temporary hardness
- (b) Permanent hardness.

## (a) Temporary Hardness

This is due to the presence of bicarbonates of calcium and magnesium. Rain water dissolves small quantities of CO<sub>2</sub> from the atmosphere forming a very dilute solution of carbonic acid. This water attacks calcium and magnesium carbonates in any rocks over which it flows and the soluble hydrogen carbonates or bicarbonates are formed.

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

Temporary hardness in water is easily removed by boiling, as the bicarbonates decompose readily and the insoluble carbonates are precipitated.

$$Ca(HCO_3)_2 \xrightarrow{Boil} CaCO_3 + H_2O + CO_2$$

$$(Insoluble)$$

$$Mg(HCO_3)_2 \xrightarrow{Boil} MgCO_3 + H_2O + CO_2$$

$$(Insoluble)$$

Temporary hardness can also be removed by Clark's process which involves the addition of slaked lime [Ca(OH)<sub>2</sub>].

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow \underbrace{2CaCO_3 + 2H_2O}_{(Insoluble)}$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow \underbrace{2CaCO_3 + Mg(OH)_2}_{(Insoluble)} + 2H_2O$$

It is essential to add only the **calculated amount** of  $Ca(OH)_2$  because **excess** will cause artificial hardness.

#### (b) Permanent Hardness

Permanent hardness is introduced when water passes over rocks containing the sulphates or chlorides of both of calcium and magnesium. This type of hardness cannot be removed by boiling or by the addition of slaked lime. Many substances are used for the removal of this type of hardness. The substances used to remove the hardness of water are known as water softeners. The various water softeners are:

(i) Washing soda: It removes both the temporary and permanent hardness by converting soluble calcium and magnesium compounds into insoluble carbonates.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$
  
 $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$   
 $Ca(HCO_3)_2 + Na_2CO_3 = CaCO_3 + 2NaHCO_3$   
(Insoluble) (Soluble)

In place of sodium carbonate, caustic soda or sodium phosphate can also be used.

$$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2 + 2NaCl$$
(Insoluble)

 $3MgSO_4 + 2Na_3PO_4 \longrightarrow Mg_3(PO_4)_2 + 3Na_2SO_4$ 
(Insoluble)

The ionic group is water soluble and the hydrocarbon group is oil soluble. The dirt particles are usually oil containing. As a consequence the hydrocarbon end of the soap is attached to and dissolve in the dirt particles, leaving the ionic end exposed to water. The net effect is to make the dirt particle disperse in the water as a stable emulsion and thus remove it from the object to be cleaned.

<sup>\*</sup>Ordinary soap is the sodium salt of fatty acids. It is used as cleaning agent. The basis for cleaning action of soaps is that they contain a long hydrocarbon chain with an ionic group at one end.

(ii) **Permutit:** Permutit is the technical name given to certain hydrated silicates of aluminium and sodium. It is obtained by fusing sodium carbonate, china clay, silica or quartz. The product is washed with water to remove soluble portion. The remaining crystalline mass sodium aluminosilicate or sodium zeolite (Na<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> xH<sub>2</sub>O) is technically called as **permutit.** The sodium ions of permutit are exchanged with calcium and magnesium ions, removing the hardness of the water, when hard water is passed through it (Fig. 5.12).

These ions can be re-exchanged by treating it with brine (NaCl) solution.

$$CaAl_2Si_2O_8 \cdot xH_2O + 2NaCl \longrightarrow Na_2Al_2Si_2O_8 \cdot xH_2O + CaCl_2$$

This method is useful for the removal of both **temporary** and **permanent** hardness of water.

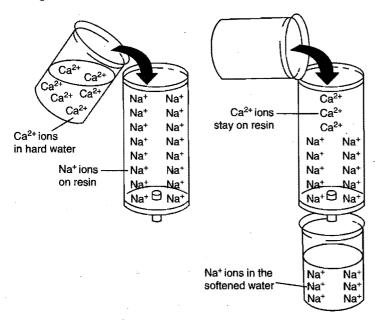


Fig. 5.12 The exchange of one type of ions in a solution by another

(iii) Calgon: The complex salt of metaphosphoric acid, sodium hexametaphosphate  $(NaPO_3)_6$ , is known as calgon. It is represented as  $Na_2[Na_4(PO_3)_6]$ . Calcium and magnesium salts present in hard water react with calgon to give complex salts.  $2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4$ 

 $2MgSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Mg_2(PO_3)_6] + 2Na_2SO_4$  $2MgSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Mg_2(PO_3)_6] + 2Na_2SO_4$ 

This method is especially used softening water for boiler use.

(iv) By ion exchange resins: Ion exchange resins are the most popular water softeners these days. These resins are synthetic substances. The cation exchanger consists of granular insoluble organic acid resin having giant molecules with —SO<sub>3</sub>H or —COOH groups while the anion exchanger contains giant organic molecules with basic groups derived from amines. Ion exchange resins remove all soluble minerals from water. The hard water is first passed through a bed of cation exchanger,

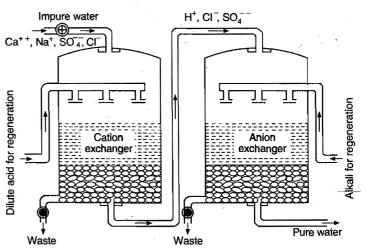


Fig. 5.13 Ion exchanger

which removes the cations like Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and others by exchanging with H<sup>+</sup> ions.

$$2RH + Ca^{2+} \longrightarrow (R)_2Ca + 2H^+$$
Resin

The water coming from cation exchanger is acidic on account of free  $H^+$ ions. This water is then passed through another bed containing anion exchanger. This exchanger removes anions like  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$  by exchanging with  $OH^-$  ions.

$$R$$
—NH<sub>3</sub>OH + Cl $\xrightarrow{}$  R—NH<sub>3</sub>Cl + OH $\xrightarrow{}$  Resin

The OH ions neutralise the H ions.

$$H^+ + OH^- = H_2O$$

This process gives distilled water and can be used in laboratories.

The cation exchanger is regenerated by the action of an acid and the anion exchanger is regenerated by pouring a solution of a suitable sodium salt through it.

#### Disadvantages of Hard Water

(i) In domestic use: Water is required for cooking, bathing and washing of clothes, etc., in our daily life. Hardness upto 100 to 150 ppm in water is tolerable, but if the hardness is more than this, the water is not suitable for domestic use. Pulses and vegetables do not cook well in hard water. Hard water spoils the lustre of utensils. Scales are formed in cooking vessels which cause wastage of fuel and cleaning of the vessels becomes difficult.

Hard water is not fit for bathing as it does not produce sufficient lather with soap. It makes the skin dry. Hard water is unfit for laundry purposes. There is a considerable loss of soap due to formation of insoluble compounds. Yellow stains are formed on the clothes if iron salts are present in hard water.

- (ii) In industrial use: Industries like dyeing, printing textiles, sugar, etc., require large quantities of water. Water containing iron and manganese salts is unfit for use in dyeing and printing textiles because these produce insoluble lakes with dyes.
- (iii) In boiler use: Water is used in producing steam. When hard water is used for production of steam in boilers, it presents three main difficulties:
- (a) Formation of scales: It is the deposition of dissolved minerals in the form of crust within the boiler shell. The crust is hard and heat insulating. It makes wastage of fuel. Sometimes the crust breaks at certain place which leads to an accident.
- **(b) Corrosion:** MgCl<sub>2</sub> present in hard water gets hydrolysed with formation of free HCl. This attacks the metal surface of the boiler and thereby shortens its life.

$$MgCl_2 + H_2O \longrightarrow Mg(OH)Cl + HCl$$

Corrosion is also affected by the presence of dissolved gases like CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, etc., in hard water. Corrosion can be prevented by the addition of suitable amounts of alkalies like NaOH or Na<sub>2</sub>CO<sub>3</sub>.

**(c) Foaming:** It is the formation of bubbles on the surface of the water in the boiler. This occurs due to the presence of suspended particles in water. It causes wastage of fuel.

## Degree of Hardness

The degree of hardness is defined as the number of parts of calcium carbonate or equivalent to various calcium and magnesium salts present in a million parts of water by mass. It is expressed as ppm.

**Example 3.** Find the degree of hardness of a sample of water containing 12 mg of MgSO<sub>4</sub> (Mol. mass 120) per kg of water.

**Solution:** 12 mg of MgSO<sub>4</sub> is present in  $10^3$ g of water. Thus,  $10^6$  g of water contains = 12000 mg of MgSO<sub>4</sub> 120 g MgSO<sub>4</sub> = 100 g of CaCO<sub>3</sub>

So, 12000 mg of MgSO<sub>4</sub> =  $\frac{100}{120} \times \frac{12000}{1000} = 10$  g CaCO<sub>3</sub>

Hardness of water = 10 ppm

**Example 4.** One litre of a sample of hard water contains 1 mg of  $CaCl_2$  and 1 mg of  $MgCl_2$ . Find the total hardness in terms of parts of  $CaCO_3$  per  $10^6$  parts of water by mass.

#### **Solution:**

Mol. mass of  $CaCl_2 = 111$ , Mol. mass of  $MgCl_2 = 95$ 111 grams of  $CaCl_2 = 100$  grams of  $CaCO_3$ 

∴ 1 mg of CaCl<sub>2</sub> 
$$\equiv \frac{100}{111} \times 1$$
 mg of CaCO<sub>3</sub>  
= 0.9 mg of CaCO<sub>3</sub>  
95 grams of MgCl<sub>2</sub>  $\equiv 100$  grams of CaCO<sub>3</sub>  
∴ 1 mg of MgCl<sub>2</sub>  $\equiv \frac{100}{95} \times 1$  mg of CaCO<sub>3</sub>  
= 1.05 mg of CaCO<sub>3</sub>

Thus, one litre of hard water contains (0.9 + 1.05) = 1.95 mg of CaCO<sub>3</sub>

One litre water =  $10^3$  grams =  $10^6$  mg Degree of hardness = 1.95 ppm

# 5.15 HYDROGEN PEROXIDE

Hydrogen peroxide was discovered by the French chemist, L.J. Thenard, in 1818, by the action of sulphuric acid on barium peroxide. It was called oxygenated water.

It occurs in traces in air, rain, snow, some natural waters and juices of certain plants.

## Laboratory Preparation

(i) From sodium peroxide: It is prepared in the laboratory by adding small amounts of sodium peroxide to ice cold water.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

In place of cold water, dilute sulphuric acid (20%) can be used. Sodium peroxide in small amounts at a time is added to cold 20% sulphuric acid.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

The crystals of hydrated sodium sulphate ( $Na_2SO_4\cdot 10H_2O$ ) are removed by cooling the solution. The solution of hydrogen peroxide obtained always consists some dissolved sodium sulphate. The concentration of  $H_2O_2$  is about 3%.

(ii) From barium peroxide: Hydrogen peroxide can be obtained by adding barium peroxide to dilute sulphuric acid at 0°C. The reaction between anhydrous barium peroxide and sulphuric acid is, however, slow and practically ceases after some time due to the formation of a protective coating of barium sulphate on barium peroxide. This difficulty can be overcome if hydrated barium peroxide is used in place of anhydrous barium peroxide.

$$BaO_2 \cdot 8H_2O + H_2SO_4 = BaSO_4 + H_2O_2 + 8H_2O$$

The barium sulphate formed is filtered off and a solution of H<sub>2</sub>O<sub>2</sub> is obtained.

The use of sulphuric acid has a disadvantage as it catalyses the decomposition of hydrogen peroxide formed. In place of sulphuric acid, weak acids like orthophosphoric acid, carbonic acid are preferred. Barium peroxide on treatment with orthophosphoric acid gives a precipitate of barium phosphate and  $H_2O_2$  which goes into the solution.

$$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 3H_2O_2$$

Insoluble barium phosphate is filtered off. The filtrate consists of hydrogen peroxide.

The barium phosphate is decomposed by dilute sulphuric acid.

$$Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4 + 2H_3PO_4$$

BaSO<sub>4</sub> is removed by filtration and orthophosphoric acid is used again.

(iii) Merck's process: H<sub>2</sub>O<sub>2</sub> can be obtained by passing a current of CO<sub>2</sub> through a cold pasty solution of barium peroxide in water.

$$BaO_2 + CO_2 + H_2O \longrightarrow BaCO_3 + H_2O_2$$

Barium carbonate being insoluble is filtered off.

#### Manufacture of Hydrogen Peroxide

(i) Auto-oxidation of 2-butyl anthraquinol: This is the most recent process for the manufacture of hydrogen peroxide. 2-Butyl anthraquinone is catalytically reduced to 2-butyl anthraquinol in an organic solvent by passing hydrogen in presence of palladium. It is then oxidised by passing air. The  $H_2O_2$  is extracted with water to give about a 20% solution. 2-Butyl anthraquinone is reformed which is again used. The method, thus, involves alternate oxidation and reduction steps, only hydrogen is consmued in this method (Fig 5.14).

$$\begin{array}{c} OH \\ C_4H_9 \\ H_2(Pd) \\ \hline \\ OH \\ 2\text{-Butyl anthraquinol} \\ \hline \\ O_2\text{(Air)} \\ \hline \\ O \\ C_4H_9 \\ + H_2O_2 \\ \hline \\ O \\ \end{array}$$

Fig. 5.14

(ii) By oxidation of isopropyl alcohol: This industrial method of manufacture of hydrogen peroxide involves the oxidation of isopropyl alcohol with oxygen under slight pressure. The isopropyl alcohol is mixed with a small amount of  $H_2O_2$  and oxygen is passed through at  $70^{\circ}$ C. The  $H_2O_2$  added acts

as an initiator. The alcohol gets oxidised giving acetone and hydrogen peroxide.

$$CH_3CHOHCH_3 + O_2 \longrightarrow CH_3COCH_3 + H_2O_2$$

Acetone and unreacted isopropyl alcohol distil over leaving behind the aqueous solution of hydrogen peroxide.

(iii) Electrolytic process: In this process, the electrolysis of 50% sulphuric acid is carried out at low temperature using platinum electrodes and a current of high density. Peroxy disulphuric acid is formed.

$$2H_2SO_4 \Longrightarrow 2H^+ + 2HSO_4^-$$
  
 $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$  (At anode)  
Peroxy  
disulphuric acid

Peroxy disulphuric acid is distilled. Hydrolysis occurs and a distillate containing about 30%  $H_2O_2$  is obtained.

$$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

In place of 50% H<sub>2</sub>SO<sub>4</sub>, ammonium hydrogen sulphate dissolved in excess of sulphuric acid can be used for electrolysis.

$$NH_4HSO_4 \Longrightarrow NH_4SO_4^- + H^+$$
**At anode**

$$2NH_4SO_4^- \longrightarrow (NH_4)_2S_2O_8 + 2e^-$$

$$Ammonium peroxy disulphate$$

At cathode 
$$2H^+ + 2e^- \longrightarrow H_2(g)$$

The solution containing ammonium peroxy disulphate is heated at 43 mm pressure when its hydrolysis occurs forming hydrogen peroxide.

$$(NH_4)_2S_2O_8 + 2H_2O \longrightarrow 2NH_4 \cdot HSO_4 + H_2O_2$$

Hydrogen peroxide along with water distils over. Ammonium bisulphate can be used again. This method gives 30-40% aqueous solution of hydrogen peroxide.

 $D_2O_2(Deutero\ peroxide)$  can also be prepared by this method.

$$K_2S_2O_8 + 2D_2O \longrightarrow 2KDSO_4 + D_2O_2$$

## Concentration of H<sub>2</sub>O<sub>2</sub> solution

Hydrogen peroxide obtained by the above methods is always in the form of dilute aqueous solution. The concentration of this solution is difficult due to explosive nature of hydrogen peroxide. The explosive decomposition is catalysed by the presence of organic matter and metallic ions. The concentration of the aqueous dilute solution having  $H_2O_2$  is done carefully by the application of following steps:

(i) The dilute solution is concentrated at 60–70°C on a water bath. Water being more volatile than hydrogen peroxide, a considerable amount of water gets evaporated and the concentration of the solution becomes 30%. It is not advisable to concentrate the solution beyond 30% as there is possibility of an explosion by this step.

(ii) The above solution is distilled at 35–40°C under reduced pressure of about 15 mm in the apparatus shown in Fig. 5.15. Repeated distillation gives 90% H<sub>2</sub>O<sub>2</sub>.

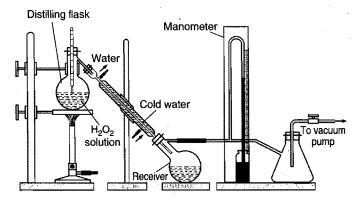


Fig. 5.15 Under low pressure concentration of H<sub>2</sub>O<sub>2</sub>

(iii) Further concentration is achieved by cooling 90% solution with the help of solid CO2 and ether bath till crystallisation sets in. Crystals are separated, melted and refrozen to get 99% pure H<sub>2</sub>O<sub>2</sub>.

#### Storing

The decomposition of  $H_2O_2$  is easily catalysed by metals, rough surfaces, sunlight, dust particles, glass and alkali. It is stored in vessels of pure aluminium or in stone jars in dark. Concentrated solutions of hydrogen peroxide are stored these days in polythene bottles kept in refrigerators. Small amounts of stabilizers such as orthophosphoric acid, acetanilide or sodium stannate are added to the solutions to be stored.

#### Properties of H<sub>2</sub>O<sub>2</sub>

Physical Properties: (i) Pure anhydrous hydrogen peroxide is a syrupy liquid. It is colourless but gives a bluish tinge in thick layers. It is odourless.

- (ii) Its specific gravity is 1.45 at 0°C.
- (iii) It is soluble in water, alcohol and ether.
- (iv) It has bitter taste. It is injurious to skin (blisters are
- (v) It boils at 152°C and freezes at -0.89°C. It begins to decompose at boiling point, however, it can be distilled under reduced pressure.
  - (vi) It is an associated liquid due to hydrogen bonding.
- (vii) The dipole moment of  $H_2O_2$  is little more (2.1 D) than that of  $H_2O$  (1.84 D).

#### **Chemical Properties:**

(i) Stability: It is unstable in nature. It decomposes on standing and heating. It is an example of auto oxidation-reduction reaction.

$$2H_2O_2 = 2H_2O + O_2$$

The oxidation number of oxygen changes to 0 and -2 from -1. Presence of traces of MnO<sub>2</sub>, carbon, alkali or finely divided metals like Pt, Au, Ag accelerate its decomposition. Traces of acid, acetanilide, alcohol or stannates increase its stability.

(ii) Acidic nature: The pure liquid has weak acidic nature but its aqueous solution is neutral towards litmus. It reacts with alkalies and carbonates to give their corresponding peroxides.

$$H_2O_2 + 2NaOH = Na_2O_2 + 2H_2O$$
  
 $H_2O_2 + Ba(OH)_2 = BaO_2 + 2H_2O$   
 $H_2O_2 + Na_2CO_3 = Na_2O_2 + CO_2 + H_2O$ 

(iii) Oxidising nature: It is a powerful oxidising agent. It is an electron acceptor in acidic and alkaline solutions.

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O$$
 (In acidic solutions)  
 $H_2O_2 + 2e^- = 2OH^-$  (In alkaline solutions)

The reactions are generally slow in acid solutions but fast in alkaline solutions.

Oxidising nature of hydrogen peroxide can be interpreted on account of the possession of labile oxygen atom. The potential equation for its oxidising nature can be written as,

$$H_2O_2 \longrightarrow H_2O + O$$

The following examples show the **oxidising nature** of  $H_2O_2$ : (a) It oxidises black lead sulphide (PbS) to white lead sulphate (PbSO<sub>4</sub>).

$$[H_2O_2 \longrightarrow H_2O + O] \times 4$$

$$PbS + 4O \longrightarrow PbSO_4$$

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O_4$$

(b) It oxidises nitrites to nitrates.

$$\begin{array}{c} H_2O_2 \longrightarrow H_2O + O \\ NaNO_2 + O \longrightarrow NaNO_3 \end{array}$$

$$\begin{array}{c} NaNO_2 + H_2O_2 \longrightarrow NaNO_3 + H_2O \end{array}$$

(c) It oxidises sulphites into sulphates.

$$H_2O_2 \longrightarrow H_2O + O$$

$$Na_2SO_3 + O \longrightarrow Na_2SO_4$$

$$Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$$

$$H_2O_2 \longrightarrow H_2O + O$$

$$Na_3AsO_3 + O \longrightarrow Na_3AsO_4$$

$$Na_3AsO_3 + H_2O_2 \longrightarrow Na_3AsO_4 + H_2O$$

(e) It liberates iodine from potassium iodide.

$$\begin{aligned} & H_2O_2 \longrightarrow H_2O + O \\ & 2KI + H_2SO_4 + O \longrightarrow K_2SO_4 + I_2 + H_2O \\ \hline & 2KI + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + I_2 + 2H_2O \end{aligned}$$
 or 
$$2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O$$

(f) It oxidises  $H_2S$  into sulphur.

$$\begin{array}{c} H_2O_2 \longrightarrow H_2O + O \\ H_2S + O \longrightarrow H_2O + S \end{array}$$

$$\begin{array}{c} H_2S + H_2O_2 \longrightarrow 2H_2O + S \end{array}$$

(g) It oxidises acidified ferrous sulphate to ferric sulphate.

$$H_2O_2 \longrightarrow H_2O + O$$

$$2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$$
or 
$$2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$$

**(h)** It oxidises acidified potassium ferrocyanide to potassium ferricyanide.

$$\begin{aligned} &H_2O_2 \longrightarrow H_2O + O \\ \frac{2K_4Fe(CN)_6 + H_2SO_4 + O \longrightarrow 2K_3Fe(CN)_6 + K_2SO_4 + H_2O}{2K_4Fe(CN)_6 + H_2SO_4 + H_2O_2 \rightarrow 2K_3Fe(CN)_6 + K_2SO_4 + 2H_2O} \\ \text{or } &2[Fe(CN)_6]^{4-} + H_2O_2 + 2H^+ \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O \end{aligned}$$

(i) It oxidises formaldehyde to formic acid. This oxidation occurs in presence of pyrogallol and in alkaline medium.

$$\begin{aligned} & \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O} \\ & \underline{ \text{HCHO} + \text{O} \longrightarrow \text{HCOOH} } \\ & \underline{ \text{HCHO} + \text{H}_2\text{O}_2 \longrightarrow \text{HCOOH} + \text{H}_2\text{O} } \end{aligned}$$
 or 
$$\begin{aligned} & \text{2HCHO} + \text{H}_2\text{O}_2 \longrightarrow \text{2HCOOH} + \text{H}_2 \end{aligned}$$

(j) Benzene in presence of ferrous sulphate is oxidised to phenol.

$$2 \bigcirc + H_2O_2 \xrightarrow{\text{FeSO}_4} 2 \bigcirc$$

(k) It dissolves the chromic hydroxide precipitate present in NaOH solution forming a yellow solution of sodium chromate.

$$[H_2O_2 \longrightarrow H_2O + O] \times 3$$

$$2Cr(OH)_3 + 4NaOH + 3O \longrightarrow 2Na_2CrO_4 + 5H_2O$$

$$2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$

(1) A solution of chromic acid in sulphuric acid or acidified potassium dichromate is oxidised to blue peroxide of chromium (CrO<sub>5</sub>) which is unstable, however, it is soluble in ether and produces blue coloured solution.

$$K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + H_2Cr_2O_7$$

$$[H_2O_2 \longrightarrow H_2O + O] \times 4$$

$$H_2Cr_2O_7 + 4O \longrightarrow 2CrO_5 + H_2O$$

$$K_2Cr_2O_7 + H_2CO_7 + H_2O_7 \longrightarrow 2CrO_7 + K_2O_7 + 5O_7$$

 $K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow 2CrO_5 + K_2SO_4 + 5H_2O_4$ 

Peroxide of chromium decomposes to form chromic sulphate and oxygen.

$$4CrO_5 + 6H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 6H_2O + 7O_2$$

Peroxide of chromium is represented as



(Butterfly shape)

(m) In alkaline medium, it oxidises manganese sulphate (a manganous salt) to manganese dioxide.

$$MnSO_4 + H_2O_2 + 2NaOH \longrightarrow MnO_2 + Na_2SO_4 + 2H_2O$$
  
or  $Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$ 

(n) In acidic solution, mercury is oxidised to mercuric oxide.

$$Hg + H_2O_2 \xrightarrow{H_2SO_4} HgO + H_2O$$

(o) Bleaching action: Due to its oxidising nature, it acts as a bleaching agent.

Coloured material + O ---- Colourless

It bleaches materials like silk, hair, ivory, cotton, wool, etc.

When used as a hair bleach (a 6% solution), it acts by oxidizing the pigments in the hair.

(iv) Reducing nature: It can also act as a reducing agent towards powerful oxidising agents.

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$$

In alkaline solution, however, its reducing action is more effective.

$$H_2O_2 + 2OH \longrightarrow 2H_2O + O_2 + 2e^-$$

The potential equation when H<sub>2</sub>O<sub>2</sub> acts as a reducing agent can be expressed as,

$$H_2O_2 + O \longrightarrow H_2O + O_2$$

(a) Ag<sub>2</sub>O is reduced to silver.

$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

(b) It reduces ozone to oxygen.

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

(c) Manganese dioxide in acidic medium is reduced to manganous salt.

$$MnO_2 + H_2SO_4 + H_2O_2 \longrightarrow MnSO_4 + 2H_2O + O_2$$

(d) Lead dioxide is reduced to lead monoxide.

$$PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$$

(e) Red lead in presence of HNO<sub>3</sub> is reduced to plumbous salt.

$$Pb_3O_4 + 6HNO_3 + H_2O_2 \longrightarrow 3Pb(NO_3)_2 + 4H_2O + O_2$$

(f) Chlorine and bromine are reduced to corresponding hydracids.

$$Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$$

This reaction can be shown in following steps:

$$\begin{array}{c} Cl_2 + H_2O \longrightarrow HCl + HClO \\ \underline{HClO + H_2O_2 \longrightarrow HCl + H_2O + O_2} \\ \hline Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2 \\ \\ Similarly \;,\;\; Br_2 + H_2O_2 \longrightarrow 2HBr + O_2 \end{array}$$

(g) It reduces acidified KMnO<sub>4</sub> solution, *i.e.*, acidified KMnO<sub>4</sub> is decolourised by H<sub>2</sub>O<sub>2</sub>.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
  
 $5H_2O_2 + 5O \longrightarrow 5H_2O + 5O_2$ 

$$2KMnO_{4} + 3H_{2}SO_{4} + 5H_{2}O_{2} \rightarrow K_{2}SO_{4} + 2MnSO_{4} + 8H_{2}O + 5O_{2}$$

or 
$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

(h) Potassium ferricyanide (alk. solution) is reduced to potassium ferrocyanide.

$$2K_3Fe(CN)_6 + 2KOH \longrightarrow 2K_4Fe(CN)_6 + H_2O + O$$
  
 $H_2O_2 + O \longrightarrow H_2O + O_2$ 

$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 \longrightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$$
  
or  $2[Fe(CN)_6]^{3-} + 2OH^- + H_2O_2 \longrightarrow 2[Fe(CN)_6]^{4-} + 2H_2O + O_2$ 

(i) Hypohalites are reduced to halides.

$$NaOCl + H_2O_2 \longrightarrow NaCl + H_2O + O_2$$

(j) KIO<sub>4</sub> is reduced to KIO<sub>3</sub>,

$$KIO_4 + H_2O_2 \longrightarrow KIO_3 + H_2O + O_2$$

(v) Addition reactions: Hydrogen peroxide is capable of adding itself to ethylenic linkage.

$$\begin{array}{cccc} CH_2 & HO & CH_2OH \\ \parallel & + & \parallel & \longrightarrow & \parallel \\ CH_2 & HO & CH_2OH \\ Ethylene & Ethylene glycol \end{array}$$

#### **Uses**

Hydrogen peroxide in the form of aqueous solution is used:

- (i) in the bleaching of delicate materials such as wool, silk, cotton, bone, ivory, hair, etc.
- (ii) as a valuable antiseptic and germicide for washing wounds, teeth and ears under the name of **perhydrol**.
- (iii) In general a 3% H<sub>2</sub>O<sub>2</sub> aqueous solution is used as a mild antiseptic. Contact of H<sub>2</sub>O<sub>2</sub> with blood catalyzes its disproportionation into oxygen and water, which cleanses the wound.
- (iv) As it oxidizes unpleasant effluents without producing any harmful by-products,  $H_2O_2$  is widely used as an oxidizing agent in the control of pollution.
  - (vi) for restoring colour of old paintings.
  - (v) as an oxidising agent in the laboratory.
- (vi) as 'antichlor' to remove traces of chlorine and hypochlorite.
- (vii) highly concentrated solution (about 40%) of  $H_2O_2$  is used to oxidise petrol, alcohol and hydrazine hydrate for the propelling of rockets and torpedoes.

$$NH_2 \cdot NH_2 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$$

The reaction is highly exothermic and is accompanied by a large increase in volume.

(vii) in the detection of Ti<sup>4+</sup>, V<sup>5+</sup> and Cr<sup>3+</sup> ions.

(viii) It is used to produce sodium peroxoborate.  $Na_2B_2(O_2)_2(OH)_4$  in hexahydrate state, it is used as a brightner in washing powders.

$$2NaBO_2 + 2H_2O_2 + 6H_2O \longrightarrow$$

$$Na_2[(OH)_2B(O-O)_2B(OH)_2]6H_2O$$

Structure of peroxoborate ion may be given as,

#### M Tests of Hydrogen Peroxide

(i) A filter paper with a stain of black lead sulphide (PbS) when brought in contact with a solution of H<sub>2</sub>O<sub>2</sub>, the black stain turns white.

$$[PbS \longrightarrow PbSO_4]$$

(ii) An acidified solution of titanium salt when treated with H<sub>2</sub>O<sub>2</sub>, yellow or orange colour is developed due to formation of pertitanic acid,

$$[Ti(SO4)2 + H2O2 + 2H2O = H2TiO4 + 2H2SO4].$$
Pertitanic acid

- (iii) H<sub>2</sub>O<sub>2</sub> when shaken with acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with little ether, blue colour is produced. This is due to the formation of peroxide of chromium (perchromic acid).
- (iv) It liberates iodine from KI solution which gives blue colour with starch solution.
- (v) It decolourises acidified potassium permanganate solution.

## Strength of H<sub>2</sub>O<sub>2</sub> solution

Strength of the sample of hydrogen peroxide is generally expressed in terms of the volume of oxygen at NTP that one volume of hydrogen peroxide gives on heating. The commercial samples are marked as '10 volume', '15 volume' or '20 volume'. '10 volume' means that one volume of hydrogen peroxide on heating gives 10 volume of oxygen at NTP. 10 mL of a '20 volume' solution of  $H_2O_2$  will liberate  $10 \times 20 = 200$  mL of oxygen at NTP.

Sometimes the concentration of  $H_2O_2$  in a solution is expressed as percentage of  $H_2O_2$  in solution, *i.e.*, g/100 mL. Thus, 30% hydrogen peroxide means that 30 g of  $H_2O_2$  is present in 100 mL of solution. '10 volume' solution of  $H_2O_2$  is 3.035% solution, *i.e.*, 3.035 g of  $H_2O_2$  present in 100 mL of the solution. This calculation can be made in the following manner.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
  
 $2(2 + 32)$  22400 mL  
= 68 g at NTP

22400 mL of oxygen is obtained at NTP from

 $= 68 \text{ g of } H_2O_2$ 

10 mL of oxygen is obtained at NTP from = 
$$\frac{68}{22400} \times 10$$
  
= 0.03035 g H<sub>2</sub>O<sub>2</sub>

1 mL of  $H_2O_2$  solution contains = 0.03035 g  $H_2O_2$ 100 mL of  $H_2O_2$  solution contains = 0.03035 × 100

$$= 3.035 g H_2O_2$$

or the solution is 3.035%

or concentration or strength of 10 volume of  $H_2O_2$  solution =  $3.035 \times 10 = 30.35$  g/litre

**Normality** of this solution can be calculated if we know the equivalent mass of hydrogen peroxide.

Equivalent mass of hydrogen peroxide  $=\frac{68}{32} \times 8 = 17.0$ 

$$\begin{bmatrix} 2H_2O_2 \longrightarrow 2H_2O + O_2 \\ 68 \text{ g} & 32 \text{ g} \end{bmatrix}$$

Number of gram equivalents in 10 volume hydrogen peroxide solution

$$= \frac{\text{concentration or strength per litre}}{\text{equivalent mass}} = \frac{30.35}{17} = 1.785$$

Normality of 10 volume solution = 1.785 N

Similarly, the concentration of '20 volume' hydrogen peroxide solution means 6.070% or 60.70 g/litre or 3.57 N.

Let volume strength is V'.

V litre O<sub>2</sub> will be given by 1 litre then at NTP

g/litre strength of 
$$H_2O_2 = \frac{68}{22.4} \times V$$

$$N = \frac{\text{Strength}}{\text{EM}} = \frac{68}{22.4} \text{ V/17} = \frac{V}{5.6}$$

i.e., Volume strength =  $5.6 \times \text{Normality}$ Similarly, Volume strength =  $11.2 \times \text{Molarity}$ 

# Structure of Hydrogen Peroxide

The vapour density as determined by Victor Meyer method at  $90^{\circ}\text{C}$  is 17. Hence, the molecular mass of  $\text{H}_2\text{O}_2$  is 34. This value has been confirmed by depression of freezing point method also. Thenard found that 17 parts by mass of hydrogen peroxide gives 9 parts by mass of water and 8 parts by mass of oxygen. Thus the empirical formula is OH and the molecular formula is  $\text{H}_2\text{O}_2$ .

Two formulae have been suggested for hydrogen peroxide.

Evidence in favour of Kingzett's formula: This formula explains the oxidising properties of  $H_2O_2$  as the oxygen linked by coordinate bond is easily lost.

$$H \longrightarrow 0 \longrightarrow H \longrightarrow 0 + 0$$

Evidence in favour of Baeyer's formula: (i) Hydrogen peroxide behaves as weak dibasic acid as one or both the hydrogen atoms can be replaced by univalent basic atoms forming salts like Na—O—O—H and Na—O—O—Na (Na<sub>2</sub>O<sub>2</sub>). This suggests that the one molecule of hydrogen peroxide consists of two hydroxyl groups.

(ii) The formation of ethylene glycol from ethylene supports Baeyer's formula.

$$\begin{array}{cccc} CH_2 - & HO & CH_2OH \\ \parallel & + & \parallel & \longrightarrow & \parallel \\ CH_2 & HO & CH_2OH \end{array}$$

It is proposed, therefore, that hydrogen peroxide is a tautomeric mixture of two forms in equilibrium.

$$H - O - O - H \longleftrightarrow H \longrightarrow O \rightarrow O$$

The calculated value of the single bond O—O distance is 1.48 Å and X-ray measurements do show that in hydrogen peroxide, O—O bond distance is  $1.46 \pm 0.03$  Å. The value of dipole moment of  $H_2O_2$  is 2.1 D. This suggests that all the four atoms do not lie in the same plane. The molecule can be pictured as lying on the spine of a book open to an angle of  $94^\circ$ . The hydrogen atoms are present one on each cover and H—O bonds making angles of  $97^\circ$  with the O—O bond as shown in Fig. 5.16. The bond distance between O—H is 0.97 Å.

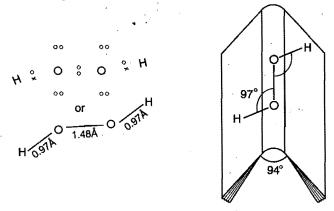


Fig. 5.16 Structure of H<sub>2</sub>O<sub>2</sub>

Structure of H<sub>2</sub>O<sub>2</sub> is slightly different in gas phase and crystalline phase.

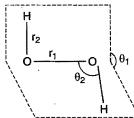


Fig. 5.17 Gas phase structure of  $H_2O_2$  (  $r_1$  = 147.5 pm,  $r_2$  = 95 pm,  $\theta_1$  = 111.5°,  $\theta_2$  = 94.8° )

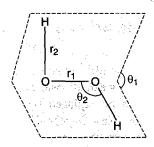


Fig. 5.18 Crystalline phase structure of  $H_2O_2$  ( $r_1=98.5$  pm,  $r_2=145.8$  pm,  $\theta_1=90.2^\circ$ ,  $\theta_2=101.9^\circ$ )

#### Example 5. Explain the following:

- (i) Why hydrated barium peroxide is used in the preparation of hydrogen peroxide instead of the anhydrous variety?
- (ii) Phosphoric acid is preferred to sulphuric acid in the preparation of  $H_2O_2$  from barium peroxide.
- (iii) Statues coated with white lead on long exposure to atmosphere turn black and the original colour can be restored on treatment with  $H_2O_2$ . [Roorkee 1987]
- **Solution:** (i) If anhydrous barium peroxide is used in the preparation, the barium sulphate, thus formed, forms an insoluble protective coating on the surface of solid barium peroxide. This prevents the further reaction of the acid, *i.e.*, causing the reaction to stop. If, however, hydrated barium peroxide (in the form of thin paste) is used, the water causes to dislodge the insoluble BaSO<sub>4</sub> from the surface of BaO<sub>2</sub>. BaSO<sub>4</sub> thus settles at the bottom of the reaction vessel and the reaction continues without any difficulty.
- (ii) When phosphoric acid is used in the preparation of  $H_2O_2$  from  $BaO_2$ , it plays the double role. It liberates  $H_2O_2$  and also acts as a preservator by retarding its decomposition.
- (iii) White lead is used as a pigment. The statues coated with white lead get blackened due to the action of  $H_2S$  present in atmosphere in traces.

$$Pb(OH)_2 \cdot 2PbCO_3 + 3H_2S \longrightarrow 3PbS + 2CO_2 + 4H_2O$$
White lead Black

When blackened statues are treated with H<sub>2</sub>O<sub>2</sub>, the PbS is oxidised to PbSO<sub>4</sub> which is colourless (white).

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$
White

#### **Example 6.** Explain the following:

- (i) Soft water lathers with soap but not hard water.
- (ii) Temporary hard water becomes soft on boiling.
- (iii) Water can extinguish most fires but not petrol fire.
- (iv) Hard water is softened before use in boilers.

**Solution:** (i) Hard water contains calcium and magnesium salts. These react with soap to form insoluble calcium and magnesium salts of fatty acids, *i.e.*, form scum and not lather.

$$2RCOONa + Ca^{2+} \longrightarrow (RCOO)_2Ca + 2Na^+$$
Soap Insoluble

$$2RCOONa + Mg^{2+} \longrightarrow (RCOO)_2Mg + 2Na^+$$

(ii) Temporary hardness of water is due to the presence of soluble bicarbonates of calcium and magnesium. On boiling, the bicarbonates are converted into insoluble carbonates which can be removed by filtration.

$$\begin{array}{c} \text{Ca}(\text{HCO}_3)_2 \longrightarrow \text{CaCO}_3 \, + \, \text{H}_2\text{O} \, + \, \text{CO}_2 \\ \\ \text{Mg}(\text{HCO}_3)_2 \longrightarrow \text{MgCO}_3 \, + \, \text{H}_2\text{O} \, + \, \text{CO}_2 \\ \\ \text{Soluble} \\ \\ \text{Insoluble} \end{array}$$

- (iii) When water poured over petrol fire, petrol being lighter than water floats over water and fire spreads instead being extinguished.
- (iv) Hard water consists bicarbonates and other soluble salts of calcium and magnesium. When hard water is evaporated in boilers, scales of precipitated carbonates of calcium and magnesium along with other salts such as sulphates, chlorides, etc., are formed. In order to avoid the formation of scales hard water is first softened before use in boilers.

#### **Example 7.** Explain the following:

- (i) A small amount of acid or alkali is added before electrolysis of water.
- (ii) The electrolysis of water for manufacturing hydrogen gas is always carried out in the presence of acid  $(H_2SO_4)$  or alkali (KOH), yet no  $SO_4^{2-}$  or  $K^{+}$  ions are discharged.
- (iii) A solution of ferric chloride acidified with HCl is unaffected when hydrogen is bubbled through it, but gets reduced when zinc is added to some acidified solution.
- (iv) When sodium hydride in fused state is electrolysed, hydrogen is discharged at anode.
- **Solution:** (i) Pure water being a weak electrolyte and feebly ionised is bad conductor of electricity. In order to make it a good conductor, a small amount of acid or alkali is added before electrolysis.
- (ii) Sulphate and potassium ions are not discharged as the discharge potential of  $SO_4^{2-}$  is much higher than  $OH^-$  ions and the discharge potential of  $K^+$  ions is much higher than  $H^+$  ions.
- (iii) Molecular (ordinary) hydrogen is not so reactive as hydrogen at the moment of formation. Zinc reacts with the acid to produce nascent hydrogen which reduces ferric chloride into ferrous chloride.
- (iv) Sodium hydride is an electrovalent compound in which hydrogen is present as an anion, H. On electrolysis, it is discharged at anode.

$$NaH \rightleftharpoons Na^{+} + H^{-}$$
Cathode
$$Na^{+} + e^{-} \longrightarrow Na$$

$$H^{-} \longrightarrow H + e^{-}$$

$$2H \longrightarrow H_{2} \uparrow$$

#### **Example 8.** What happens when?

(a) An alkaline solution of potassium ferricyanide is reacted with  $H_2O_2$ .

- (b) Hydrogen peroxide is added to acidified potassium permanganate.
- (c) Hydrogen peroxide is added to ferrous ammonium sulphate solution. [Roorkee 1985]
- (d) Chromium hydroxide is treated with hydrogen peroxide in the presence of sodium hydroxide. [M.L.N.R. 1992]
- (e) Concentrated caustic potash solution is spilled on granulated zinc.
  - (f) Hydrolith is treated with water.
  - (g) Heavy water reacts with aluminium carbide.

#### Solution:

(a) Potassium ferricyanide is reduced to potassium ferrocyanide.

$$2K_3Fe(CN)_6 + 2KOH \longrightarrow 2K_4Fe(CN)_6 + H_2O + O$$
  
 $H_2O_2 + O \longrightarrow H_2O + O_2$ 

$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 \longrightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$$

(b) Potassium permanganate is decolourised due to reduction.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$[H_2O_2 + O \longrightarrow H_2O + O_2] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow$$

$$K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

(c) Ferrous ammonium sulphate is oxidised to ferric salt.

(d) Chromium hydroxide is converted into soluble yellow sodium chromate.

$$[H_2O_2 \longrightarrow H_2O + O] \times 3$$
 
$$2Cr(OH)_3 + 4NaOH + 3O \longrightarrow 2Na_2CrO_4 + 5H_2O$$

$$2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$

(e) Zinc dissolves in caustic potash solution evolving hydrogen.

$$Zn + 2KOH \longrightarrow K_2ZnO_2 + H_2\uparrow$$

(f) Hydrolysis of CaH2 occurs with evolution of H2.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2\uparrow$$

(g) Deuteromethane is evolved.

$$Al_4C_3 + 12D_2O \longrightarrow 4Al(OD)_3 + 3CD_4$$
Heavy water Deuteromethan

**Example 9.** A 5.0 cm<sup>3</sup> solution of  $H_2O_2$  liberates 0.508 g of iodine from acidified KI solution. Calculate the strength of  $H_2O_2$  solution in terms of volume strength at STP. [I.I.T. 1995]

**Solution:** 

$$H_2O_2 + H_2SO_4 + 2KI \longrightarrow K_2SO_4 + I_2 + 2H_2O_34 g$$
  
= 254 g

254 g of I<sub>2</sub> is obtained from 34 g H<sub>2</sub>O<sub>2</sub>

0.508 g of I<sub>2</sub> is obtained from H<sub>2</sub>O<sub>2</sub> = 
$$\frac{34}{254} \times 0.508$$
  
= 0.068 g

5 mL of the solution contains =  $0.068 \text{ g H}_2\text{O}_2$ 

1 mL of the solution contains 
$$=\frac{0.068}{5}$$
 g H<sub>2</sub>O<sub>2</sub>  
= 0.0136 g H<sub>2</sub>O<sub>2</sub>

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
 $68 \text{ g}$   $22400 \text{ mL}$ 

68 g of  $H_2O_2$  gives oxygen at STP = 22400 mL 0.0136 g of  $H_2O_2$  will give oxygen at STP

$$= \frac{22400}{68} \times 0.0136$$
$$= 4.48 \text{ mL}$$

i.e., 1 mL of H<sub>2</sub>O<sub>2</sub> solution gives 4.48 mL of oxygen.

So, strength of  $H_2O_2$  solution = 4.48 volume.

Example 10. Calculate the hardness of water sample which contains 0.001 mole of MgSO<sub>4</sub> dissolved per litre of water.

$$0.001 \text{ mole } MgSO_4 = 0.001 \times 120 \text{ g } MgSO_4$$
  
=  $0.120 \text{ g } MgSO_4$ 

We know that, 
$$120 \text{ g MgSO}_4 \equiv 100 \text{ g CaCO}_3$$

So, 
$$0.120 \text{ g MgSO}_4 \equiv 0.1 \text{ g CaCO}_3$$

 $10^3$  g of water (one litre) contains = 0.1 g CaCO<sub>3</sub>

$$10^6$$
 g of water contains =  $\frac{0.1}{10^3} \times 10^6$  = 100 g CaCO<sub>3</sub>

So, the hardness of water = 100 ppm

**Example 11.** Aqueous solution of an inorganic compound (x) shows the following reactions:

- (i) It decolourises an acidified  $KMnO_4$  solution accompanied by the evolution of oxygen.
  - (ii) It liberates iodine from an acidified KI solution.
- (iii) It gives a brown precipitate with alkaline  $KMnO_4$  solution with evolution of oxygen.
  - (iv) It removes black stains from old oil paintings.

Identify, (x) and give chemical equations for the reactions at steps (i) to (iv). [Roorkee 1993]

**Solution:** In reactions (i) and (iii) (x) acts as a reducing agent while in reaction (ii) it acts as an oxidising agent. Thus, these reactions indicate that (x) is  $H_2O_2$  which is further confirmed from reaction (iv).

$$\underbrace{K_2SO_4 + 2MnSO_4}_{Soluble, colourless} + 8H_2O + 5O_2$$

(ii) 
$$2KI + H_2SO_4 + H_2O_2 \rightarrow K_2SO_4 + I_2 + 2H_2O$$

(iii) 
$$2\text{KMnO}_4 + 3\text{H}_2\text{O}_2 \rightarrow 2\text{KOH} + 2\text{MnO}_2 + 2\text{H}_2\text{O} + 3\text{O}_2$$

Brown

(iv) PbS + 
$$4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$
Black White

**Example 12.** Hydrogen peroxide acts both as an oxidising and as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of  $H_2O_2$  using chemical equations. [I.I.T. 1998]

**Solution:** Chromium hydroxide is oxidised by  $H_2O_2$  in presence of NaOH into sodium chromate

$$[H_2O_2 \longrightarrow H_2O + O] \times 3$$

$$2Cr(OH)_3 + 4NaOH + 3O \longrightarrow 2Na_2CrO_4 + 5H_2O$$

$$2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$

Potassium ferricyanide is reduced to ferrocyanide in presence of KOH by  $H_2O_2$ .

$$2K_3Fe(CN)_6 + 2KOH \longrightarrow 2K_4Fe(CN)_6 + H_2O + O$$
  
 $H_2O_2 + O \longrightarrow H_2O + O_2$ 

$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 \longrightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$$

- **Example 13.** (a) A mixture of hydrazine and  $H_2O_2$  with Cu(II) catalyst is used a rocket propellant. Why?
- (b) Can concentrated  $H_2SO_4$  be used for drying  $H_2$  gas? Justify.
- (c) The process  $\frac{1}{2}H_2(g) + e \longrightarrow H^-(g)$  is endothermic  $(\Delta H = +151 \text{ kJ mol}^{-1})$ , yet salt like hydrides are known. How do you account for this?

**Solution:** (a) The reaction between hydrazine and  $H_2O_2$  is highly exothermic and is accompanied by a large increase in the volume of the products. Hence, the mixture is used as rocket propellant.

$$N_2H_4(l) + 2H_2O_2(l) \xrightarrow{Cu(II)} N_2(g) + 4H_2O(g)$$

- (b) Concentrated  $H_2SO_4$  cannot be used for drying  $H_2$  gas as the absorption of moisture by  $H_2SO_4$  is highly exothermic in nature. The heat so produced causes hydrogen to catch fire as hydrogen is highly inflammable.
- (c) Alkali and alkaline earth metals combine with hydrogen and form ionic hydrides in spite of the fact that formation of  $H^-$  ions is an endothermic process. This is due to the reason that high lattice enthalpy released during formation of solid hydride from  $M^+$  or  $M^{2+}$  and  $H^-$  ions is more than needed for the formation of  $H^-$  ions from  $H_2$ .

**Example 14.** (a) Compare the structures of  $H_2O$  and  $H_2O_2$ . (b) Do you expect different products in solution when  $AlCl_3$  is treated separately with (i) normal water, (ii) acidified water and (iii) alkaline water?

**Solution:** (a)  $H_2O$  has a bent structure with HOH bond angle is  $104.5^{\circ}$ .  $H_2O_2$  has an open book structure with H—O—O angle equal to  $94.8^{\circ}$  and dihedral angle equal to  $111.5^{\circ}$  in gaseous phase.



(b) AlCl<sub>3</sub> is a salt of a weak base and a strong acid. In normal water, it undergoes hydrolysis.

$$AlCl_3(s) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3HCl(aq)$$
Base Acid

In acidic water,  $H^+$  ions react with Al(OH)<sub>3</sub> giving Al<sup>3+</sup>(aq) ions.

$$AlCl_3(s) \xrightarrow{\text{Acidified}} Al^{3+}(aq) + 3Cl^{-}(aq)$$

In alkaline water,  $Al(OH)_3$  reacts to form soluble tetrahydroxo-aluminate complex or meta-aluminate ions  $[AlO_2^-(aq)]$ .

$$Al(OH)_3 + OH^-(aq) \longrightarrow [Al(OH)_4]^-(aq) \text{ or } AlO_2^-(aq) + 2H_2O$$

$$AlCl_3(s) \xrightarrow{Alkaline} AlO_2^-(aq) + 2H_2O(l) + 3Cl^-(aq)$$

**Example 15.** Would you expect the hydrides of N, O and F to have lower boiling points than the hydrides of their subsequent group members? Give reasons.

**Solution:** On the basis of molecular masses of NH<sub>3</sub>, H<sub>2</sub>O and HF, their boiling points are expected to be lower than subsequent group member hydrides. However, on account of high electronegativity of N, O and F, the magnitude of hydrogen bonding is appreciable in their hydrides, *i.e.*, aggregation of molecules occurs. Hence, the boiling points of NH<sub>3</sub>, H<sub>2</sub>O and HF will be higher than the hydrides of their subsequent group members.

**Example 16.** What do you understand by (i) electron deficient (ii) electron precise and (iii) electron rich compounds of hydrogen? Provide justification with suitable examples.

**Solution:** (i) The hydrides which do not possess sufficient number of valence electrons to form normal covalent bonds, are termed electron deficient hydrides. Examples are the hydrides of group 13 such as BH<sub>3</sub>, AlH<sub>3</sub>, etc. They generally exist in polymeric forms.

- (ii) The hydrides which possess exact number of electrons to form covalent bonds are termed electron precise hydrides. Examples are the hydrides of group 14 such as CH<sub>4</sub>, SiH<sub>4</sub>, GeH<sub>4</sub>, etc.
- (iii) The hydrides which have lone pair or pairs of electrons, *i.e.*, have more electrons than required to form normal covalent bonds are termed electron rich hydrides. Examples are the hydrides of group 15, 16 and 17 such as NH<sub>3</sub>, H<sub>2</sub>O, HF, etc.

**Example 17.** What do you understand by the term non-stoichiometric hydrides? Do you expect these types of hydrides to be formed by alkali metals? Justify your answer.

**Solution:** The hydrides in which the ratio of the metal and hydrogen is found to be fractional are called non-stoichiometric hydrides. It is also observed that this fractional ratio is not fixed

but varies with the temperature and pressure. Such hydrides are formed by d- and f-block elements. In these hydrides, hydrogen atoms occupy holes in the metal lattice. Usually all the holes are not occupied, *i.e.*, some holes always remain vacant and thus, these compounds are non-stoichiometric.

Alkali metals do not form non-stoichiometric hydrides as each sodium atom loses its valency electron which is accepted by hydrogen atom to form H<sup>-</sup> ion. In this way, an ionic compound, Na<sup>+</sup> H<sup>-</sup>, is formed.

# O

# **SUMMARY AND IMPORTANT POINTS TO REMEMBER**



- 1. Hydrogen is the lightest element. Its atom consists of a single proton and a single planetary electron. Hydrogen is the only element whose atom does not have neutrons in its nucleus. It has the simplest electronic configuration,  $1s^1$ .
- Hydrogen was prepared by Cavendish in 1766 by the action of acids on metals. It was named 'inflammable air'. Lavoiser named it hydrogen (hydra = water, gennas = maker) meaning water maker.
- 3. Hydrogen is the most abundant element in the universe (70% of the universe's total mass). Sun and some other stars consist mostly of hydrogen. Free hydrogen is present in minute quantity in air, volcanic gases and natural gas. In the combined state, it constitutes 15.4% of the earth's crust and oceans as water, mineral oil, organic materials such as hydrocarbons, carbohydrates, fats, proteins, etc. Hydrogen is an essential constituent of all acids and alkalies.
- 4. Hydrogen shows dual nature. It behaves as electropositive element like alkali metals as it can lose the planetary electron. It also behaves as an electronegative element like halogens as it can gain one more electron to saturate 1s subshell. It is the first member in the periodic table but its position is not fixed. Sometimes, it is placed with alkali metals in IA subgroup and sometimes with halogens in VIIA (17th) subgroup.
- The atomic form of hydrogen exists only at high temperatures. Normal elemental hydrogen is the diatomic molecule, called dihydrogen, H<sub>2</sub>.
  - The ordinary hydrogen at room temperature is a mixture of ortho-form and para-form in the ratio of 3:1. The nuclei of ortho hydrogen spin in the same direction while that of the para hydrogen spin in the opposite directions.
- 6. Hydrogen exists in three isotopes. It is the only known element whose isotopes have the unique mass ratio of 1, 2, 3 (<sup>1</sup><sub>1</sub>H; <sup>2</sup><sub>1</sub>H; <sup>3</sup><sub>1</sub>H). The predominant form is <sup>1</sup><sub>1</sub>H (protium). <sup>2</sup><sub>1</sub>H or D (Deuterium) is present upto 0.0156% in terrestrial hydrogen, mostly in the form of HD. Tritium (Tor <sup>3</sup><sub>1</sub>H) is radioactive. It emits β-particles and its half life period is 12.33 years. The three isotopes have same chemical properties but their physical properties are different due to different atomic masses. Deuterium and tritium are used as tracers, bombarding projectiles especially in fusion reactions, i.e., in hydrogen bombs.
- There are three main sources from which dihydrogen (ordinary hydrogen) may be prepared. These are (i) Water, (ii) Acids and (iii) Alkalies.
  - (a) Alkali and alkaline earth metals react with cold water producing dihydrogen. The reactions are vigorous. To minimise the rate of reactions, usually amalgams are used.

- (b) Metals like Zn, Fe, Mn, Co, Cr, Sn, etc., decompose steam or hot water forming dihydrogen.
- (c) Reactions of steam on hydrocarbons or coke at high temperatures produce dihydrogen.

temperatures produce dinydrogen.

$$C_nH_{2n+2} + nH_2O \xrightarrow{1270 \text{ K}} nCO + (2n+1)H_2$$
 $C + H_2O \xrightarrow{\text{Cotalyst}} CO + H_2$ 

Water containing a small amount of acid or all

- (d) Water containing a small amount of acid or alkali on electrolysis in an electrolytic cell produces dihydrogen at cathode. The cathode used is usually of iron and anode usually of nickel. The two electrodes are separated by an asbestos diphragm.
- (e) Ionic hydrides on hydrolysis with water evolve dihydrogen.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$
  
Hydrolith

- (f) The metals which occupy their position above hydrogen in the electrochemical series such as Zn, Al, Mg, Fe, etc., react with dil.HCl or dil. H<sub>2</sub>SO<sub>4</sub> to evolve dihydrogen. Mn and Mg react with dil. HNO<sub>3</sub> to evolve dihydrogen.
- (g) Zn, Al, Sn, Si, Pb react with boiling NaOH or KOH to evolve dihydrogen. Uyeno's method is used for military purposes for rapid and pure production of dihydrogen when scrap aluminium reacts with caustic potash.

$$2A1 + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2$$

- (h) Dihydrogen is produced in the laboratory by action of dilute H<sub>2</sub>SO<sub>4</sub> on granular zinc. The dihydrogen produced contains a number of impurities. To remove these impurities, the evolved dihydrogen is passed through three bottles containing AgNO<sub>3</sub> solution (removes PH<sub>3</sub> and AsH<sub>3</sub>), Pb(CH<sub>3</sub>COO)<sub>2</sub> solution (removes H<sub>2</sub>S) and KOH solution (removes CO<sub>2</sub>, SO<sub>2</sub> and oxides of nitrogen) respectively.
- (i) Pure dihydrogen is obtained either (i) by carrying electrolysis of barium hydroxide solution using platinum electrodes or nickel electrodes or (ii) by action of water on sodium hydride (NaH) or (iii) by Uyeno's method.
- 8. Large quantities of dihydrogen are required these days in industry for various purposes. About 77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

Natural gas mainly consists of methane. Dihydrogen is obtained from natural gas either by partial oxidation or cracking. Natural gas is mixed with steam and passed over a

catalyst (Ni-Cr alloy) at 1200 K. The CO is converted into CO<sub>2</sub> by passing the gases and steam over iron oxide or cobalt oxide catalyst at 750 K resulting in the generation of more H<sub>2</sub>.

$$CH_4 + H_2O \xrightarrow[Ni-Cr]{1200 \text{ K}} CO + 3H_2$$

$$CH_4 \xrightarrow{Cracking} C + 2H_2$$

$$CO + H_2O \xrightarrow[Fe_2O_3]{750 \text{ K}} CO_2 + H_2$$

(CO<sub>2</sub> is removed by dissolving it in water under pressure of about 25-30 atmosphere.)

Bosch's process is used to obtain dihydrogen from coke.

$$C + H_2O \xrightarrow{1273 \text{ K}} CO + H_2$$

- 9. Dihydrogen is a colourless, odourless and tasteless gas. Hydrogen has high heat of dissociation (436 kJ mol<sup>-1</sup>). This property is made use of in the atomic torch which generates temperatures of about 4000 K and is ideal for welding of metals of high melting points. It has low melting and boiling points. It is only slightly soluble in water. It is diatomic in nature and bond length is 74 pm.
- 10. Certain metals like palladium, platinum, iron, etc., can adsorb large quantities of hydrogen. The adsorbed hydrogen is called occluded hydrogen. This property can be used for the purification of hydrogen because only pure hydrogen is adsorbed.
- 11. Dihydrogen is inflammable or combustible gas. However, it does not help in burning. It burns with blue flame in oxygen atmosphere forming water. Dihydrogen is not a very active element and does not react readily with other elements. Under suitable conditions, it can be made to combine with metals and non-metals both. It forms compounds by losing, gaining or sharing of its only electron. It shows oxidation states of +1, 0 and -1. H<sub>2</sub> has great affinity for oxygen. Thus, it acts as a reducing agent. The oxides of less electropositive metals such as copper, tin, iron, lead, etc., are reduced to the metals when heated in hydrogen. Numerous substances are hydrogenated in presence of suitable catalysts.
- 12. Dihydrogen forms three types of hydrides: ionic, covalent and interstitial. Ionic or salt like (saline) hydrides are formed by alkali metals, alkaline earth metals with exception of Be and Mg and some highly electropositive members of lanthanide series. These are colourless crystalline compounds with electrovalent nature in which hydrogen acts as an anion. All ionic hydrides react with H<sub>2</sub>O to produce dihydrogen. Ionic hydrides are powerful reducing agents.

Covalent or molecular hydrides are formed by all the true nonmetals (except zero group elements) and the elements such as Al, Ga, Sn, Pb, Sb, Bi, Po, etc., which are normally metallic in nature, *i.e.*, *p*-block elements. In these hydrides, hydrogen atoms are covalently bonded to the central atom. The boiling points of the simple hydrides of first elements of group 15 (NH<sub>3</sub>), 16 (H<sub>2</sub>O) and 17 (H<sub>2</sub>F<sub>2</sub>) are abnormally high due to intermolecular hydrogen bonding. The boiling points of remaining hydrides within the group, however, increase regularly with increase in atomic number of the element. Metallic or interstitial hydrides are formed by many d-block and f-block elements at elevated temperatures. These hydrides are often non-stoichiometric and have metallic appearance. They possess reducing properties probably due to presence of free hydrogen. These hydrides are used for the ultrapurification of hydrogen and as hydrogen storage media.

- Complex metal hydrides such as LiAlH<sub>4</sub> and NaBH<sub>4</sub> are powerful reducing agents and are widely used in organic reactions.
- 14. Hydrogen has been considered as one of the alternate sources of energy. The advantage of using hydrogen as a fuel is that it is environmentally clean. The second advantage with hydrogen is that the heat of combustion of hydrogen per gram is higher than any other fuel. Our energy needs can be met by gaseous, liquid and solid hydrogen. However, cheaper methods of production of hydrogen are to be developed and problems in storing and transportation are to be tackled.
- 15. Dihydrogen has following industrial applications:
  - (a) Synthesis of ammonia
  - (b) Manufacture of methyl alcohol
  - (c) Hydrogenation of oils
  - (d) Manufacture of hydrogen chloride
  - (e) Production of synthetic petrol
  - (f) Oxy-hydrogen flame
  - (g) Fuel for rockets
  - (h) With helium, it is used for filling balloons employed for atmospheric study
- 16. Water is most common and abundant compound of hydrogen. Water occupies the major part of the earth. It is essential to life. Two-third of human body is water. Water has the ability to dissolve a number of substances. Water has unique properties. Its transformation from liquid to solid and to gaseous states is easy. Water exists as a liquid under normal atmospheric conditions. It exists as a solid below 0°C and as a gas above 100°C. The unique properties in the liquid and solid phase are a result of extensive hydrogen bonding between water molecules. Water molecule forms four H-bonds. Water has a higher specific heat, thermal conductivity and surface tension than most of the other liquids. Because of these properties water plays an important role in the biosphere. The density of water is maximum at 4°C.
- 17. Pure water is colourless, tasteless and odourless. It is neutral in nature, pH of pure water is 7. It reacts with active metals when hydrogen is evolved. It is decomposed by metals like Zn, Mg, Fe, etc., when steam is passed over hot metals. Fluorine decomposes water forming ozonised oxygen. Chlorine decomposes water in presence of sunlight. Acidic oxides combine with water to form oxy-acids while basic oxides form alkalies. Water decomposes a number of hydrides, carbides, nitrides, phosphides with liberation of hydrogen, acetylene (or methane), ammonia, phosphine, respectively. Water forms hydrates of different types.
- 18. Oxygen atom in water molecule is sp<sup>3</sup> hybridized, four hybrid orbitals directed towards the corners of a tetrahedron are formed. Two of the hybrid orbitals having one electron each overlap with hydrogen atoms and form two sigma bonds. Thus, the molecule has a bent (V-shaped) structure with a

bond angle of 104.5°. The bond angle is less than the expected due to presence of two lone pairs of electrons on two uncombined hybrid orbitals. The molecule is polar due to difference in the electronegativities of hydrogen and oxygen and possesses dipole moment. Water molecules are linked with each other by hydrogen bonding.

- 19. Ice has open cage like structure with a number of vacant spaces in the crystal lattice. As a result, the density of ice is lower than that of water.
- 20. Water is tested by the following tests:
  - (i) A drop of water when added to anhydrous copper sulphate, change its colour from white to blue.
  - (ii) Water reacts with calcium carbide to evolve acetylene which burns with bright flame.
- 21. Water is said to be soft if it produces sufficient lather with soap. Hard water does not form lather readily with soap as it forms an insoluble scum. Hardness of water is of two types:
  - (i) **Temporary:** This is due to presence of bicarbonates of calcium and magnesium. It can be easily removed by boiling or by adding slaked lime.
  - (ii) Permanent: It is caused by the presence of chlorides and sulphates of calcium and magnesium. Many substances can be used for the removal of permanent hardness. Those are termed water softeners. The various water softeners are:
    - (i) Washing soda (ii) Permutit—hydrated silicates of aluminium and sodium (Na<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>·XH<sub>2</sub>O) (iii) Calgon-sodium hexa-meta-phosphate (NaPO<sub>3</sub>)<sub>6</sub> (iv) Ion-exchange resins.
- 22. Degree of hardness is defined as the number of parts of calcium carbonate or equivalent to calcium and magnesium salts present in million parts of water by mass. It is expressed in ppm.
- 23. Heavy water (D<sub>2</sub>O) was discovered by Urey. One part of heavy water is present in 6000 parts of ordinary water. It is obtained by repeated electrolysis of water containing alkali. Like ordinary water, it is also colourless, odourless and tasteless. Nearly all the physical constants are higher than the corresponding values of ordinary water. It is used as a moderator in nuclear reactors.
- 24. Hydrogen peroxide was discovered by Thenard on treating barium peroxide with sulphuric acid. It was called oxygenated water.
- **25.** H<sub>2</sub>O<sub>2</sub> is prepared by adding ice cold dilute H<sub>2</sub>SO<sub>4</sub>(20%) on Na<sub>2</sub>O<sub>2</sub> or BaO<sub>2</sub>. As H<sub>2</sub>SO<sub>4</sub> catalyses the decomposition, some weaker acids such as H<sub>3</sub>PO<sub>4</sub> or H<sub>2</sub>CO<sub>3</sub> (H<sub>2</sub>O + CO<sub>2</sub>) are preferred.
- **26.** Manufacture of H<sub>2</sub>O<sub>2</sub> is done by following methods:
  - (i) Auto-oxidation of 2-butyl anthraquinol. It is the most recent method. 2-butyl anthraquinone is catalytically reduced to 2-butyl anthraquinol in an organic solvent in presence of palladium by passing hydrogen. It is then oxidised by passing air. The H<sub>2</sub>O<sub>2</sub> is extracted with water to give a 20% solution. 2-butyl anthraquinone is reformed which is again used.
  - (ii) By oxidation of isopropyl alcohol: The isopropyl alcohol is mixed with a small amount of H<sub>2</sub>O<sub>2</sub> and oxygen is passed at 70°C. Acetone and unreacted

- alcohol distil over leaving behind the aqueous solution of  $H_2O_2$ .
- (iii) Electrolytic process: 50% H<sub>2</sub>SO<sub>4</sub> solution or equimolar mixture of H<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is electrolysed at low temperature using platinum electrodes and a current of high density. Peroxy disulphuric acid (H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) or ammonium peroxy disulphate is formed which on hydrolysis gives H<sub>2</sub>O<sub>2</sub> solution.
- 27. H<sub>2</sub>O<sub>2</sub> is stored in the vessels of pure aluminium or in stone jars in dark. Concentrated solutions of H<sub>2</sub>O<sub>2</sub> are stored these days in polythene bottles kept in refrigerators. Small amounts of stabilizers such as orthophosphoric acid acetanilide or sodium stannate are added.
- **28.** Pure H<sub>2</sub>O<sub>2</sub> is a syrupy liquid. It is soluble in water, alcohol and ether. Its specific gravity is 1.45. It is injurious to skin. It has bitter taste. Hydrogen bonding is present, thus it is an associated liquid.
- 29. It decomposes on standing and heating. Presence of traces of MnO<sub>2</sub>, carbon, alkali or finely divided metals like Pt, Au, Ag, etc., accelerate its decomposition. The pure liquid-has-weak acidic nature.  $K_a = 1.55 \times 10^{-12}$ . It is less acidic than carbonic acid, i.e.,  $H_2CO_3 > H_2O_2 > H_2O$ . It acts as an oxidising agent as well as a reducing agent both in the acidic as well as in the basic medium.

$$\begin{aligned} & \text{Oxidising nature} \begin{cases} \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e & \longrightarrow 2\text{H}_2\text{O} \text{ (In acidic medium)} \\ \text{H}_2\text{O}_2 + 2e & \longrightarrow 2\text{OH}^- \text{ (In alkaline medium)} \end{cases} \\ & \text{Reducing nature} \begin{cases} \text{H}_2\text{O}_2 & \longrightarrow 2\text{H}^+ + \text{O}_2 + 2e \\ & \text{ (In acidic medium)} \end{cases} \\ & \text{H}_2\text{O}_2 + 2\text{OH}^- & \longrightarrow 2\text{H}_2\text{O} + \text{O}_2 + 2e \\ & \text{ (In alkaline medium)} \end{cases}$$

**30.** H<sub>2</sub>O<sub>2</sub> acts as a bleaching agent for delicate articles like hair, silk, wool, ivory, etc. The bleaching action is due to oxidation by nascent oxygen and hence is permanent.

$$H_2O_2 \longrightarrow H_2O + [O]$$

- **31.** H<sub>2</sub>O<sub>2</sub> is a valuable antiseptic and germicide for washing wounds teeth and ears under the name **perhydrol**. It is used for restoring colour of old paintings as it oxidises black PbS to PbSO<sub>4</sub>. Highly concentrated solutions (about 40%) of H<sub>2</sub>O<sub>2</sub> are used to oxidise petrol, alcohol, hydrazine hydrate for the propelling rockets and torpedoes.
- 32. X-ray measurements show that bond distance between O—O is  $1.46 \pm 0.03$  Å. The value of dipole moment is 2.1D. This suggests that  $H_2O_2$  molecule is a non-linear molecule. In gas phase, the molecule can be pictured as lying on the spine of the book open to an angle of  $111.5^{\circ}$ . The hydrogen atoms are present on each cover and  $\angle OOH = 94.8^{\circ}$ .
- **33.** Strength of the sample of hydrogen peroxide is generally expressed in terms of volume of oxygen at NTP that one volume of hydrogen peroxide on heating gives. The commercial samples are marked as '10 volume', '15 volume' or '20 volume'. '10 volume' solution means that one volume of H<sub>2</sub>O<sub>2</sub> gives 10 volume of oxygen at NTP on decomposition. Sometimes the concentration of H<sub>2</sub>O<sub>2</sub> is expressed as percentage of H<sub>2</sub>O<sub>2</sub> in solution, *i.e.*, g/100 mL. 30% hydrogen

peroxide means that 30 grams of H<sub>2</sub>O<sub>2</sub> is present in 100 mL of solution.

'10 volume' solution of  $H_2O_2$  is 3.035% solution. Strength of '10 volume'  $H_2O_2$  solution is 30.35 g/litre. Normality of '10 volume'  $H_2O_2$  solution = 1.785 *i.e.*, Volume strength =  $5.6 \times Normality$ Similarly Volume strength =  $11.2 \times Molarity$ .

 $1M H_2O_2 = 2N H_2O_2 = 11.2 \text{ volume } H_2O_2 = 3.4\%$ 

# ••- PRACTICE PROBLEMS -

#### **■** Subjective Type Questions

#### 1. Answer the following:

- (a) Which isotope of hydrogen contains equal number of protons and neutrons?
- (b) What is Syn. gas?
- (c) Name two complex metal hydrides which are used as reducing agents in organic reactions.
- (d) What is hydride gap?
- (e) What is autoprotolysis of water?
- (f) What common compounds of hydrogen are more powerful reducing agents than hydrogen itself?
- 2. (a) Which is heavier, ice or water?
  - (b) What is deionised water? Can distilled water be called as deionised water?
  - (c) What name is given to a water softener, sodium polymetaphosphate?
  - (d) What gases are evolved when the following react with water?
    - (i)  $Mg_3N_2$  (ii)  $CaC_2$  (iii)  $Ca_3P_2$
- 3. (a) Give three characteristics in which hydrogen resembles halogens.
  - (c) Give three characteristics in which hydrogen resembles alkali metals.
  - (c) Give four industrial uses of hydrogen.

#### 4. Answer the following:

- (i) In which group of the periodic table, hydrogen is placed?
- (ii) Which metals react with H<sub>2</sub>O or dilute HCl or dilute H<sub>2</sub>SO<sub>4</sub> to evolve hydrogen?
- (iii) Very pure hydrogen is obtained with rapidity by the action of caustic potash on scrap aluminium. What is the name of this method?
- (iv) Which zinc (pure or commercial) is used for the preparation of hydrogen in laboratory?
- (v) Which solution is used for the removal of AsH<sub>3</sub> and PH<sub>3</sub> present in very small amounts in hydrogen sample?
- (vi) How is hydrogen obtained from natural gas?
- (vii) What type of hydrides are formed by the elements having low electronegativity?
- (viii) What is the temperature of oxy-hydrogen flame?
- (ix) What is percentage of ortho form in ordinary hydrogen at room temperature?
- (x) Which form of hydrogen is used for welding purposes?
- (xi) Which isotope of hydrogen is radioactive in nature?
- (xii) What is the use of heavy water in nuclear reactors?

- (xiii) What is the difference between the rates of reactions of D<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>?
- (xiv) How heavy water is obtained from ordinary water?
- (xv) Why has D<sub>2</sub>O more density than H<sub>2</sub>O?
- (xvi) What chemical change does occur when temporary hard water is boiled?
- (xvii) What is calgon?
- (xviii) What type of overlapping of orbitals occur in the formation of peroxo linkage (—O—O—) in H<sub>2</sub>O<sub>2</sub> molecule?
- (xix) Name the chemical compound used in the preparation of H<sub>2</sub>O<sub>2</sub> by auto-oxidation.
- (xx) Name the blue coloured compound formed in the reaction of H<sub>2</sub>O<sub>2</sub> with acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in ether.
- (xxi) How H<sub>2</sub>O<sub>2</sub> acts as an antiseptic?
- (xxii) What volume of oxygen at NTP is obtained from 10 mL of 10 volume H<sub>2</sub>O<sub>2</sub>?
- (xxiii) What is the principle in bleaching action of H<sub>2</sub>O<sub>2</sub>?
- (xxiv) How is concentration of H<sub>2</sub>O<sub>2</sub> done?
- (xxv) Which acts as an oxidising agent in the reaction of H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>?

#### 5. What happens when?

- (a) An alkaline solution of potassium ferricyanide is treated with hydrogen peroxide. [I.I.T. 1989]
- (b) Chromium hydroxide is treated with hydrogen peroxide in the presence of NaOH. [M.L.N.R. 1992]
- (c) Concentrated solution of NH<sub>4</sub>HSO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> is electrolysed using current of high density.
- (d) Hydrazine reacts with hydrogen peroxide.
- (e) Benzene is treated with H<sub>2</sub>O<sub>2</sub> in presence of FeSO<sub>4</sub>.
- (f) Lactic acid is treated with Fenton's reagent.
- (g) Tin tetrahalide is treated with lithium aluminium hydride.
- (h) Sodium hydride reacts with diborane.
- (i) Hydrogen peroxide reacts with Ba(OH)<sub>2</sub>.
- (j) Sodium hypochlorite reacts with H<sub>2</sub>O<sub>2</sub>.
- (i) Give two reactions in each case to show that H<sub>2</sub>O<sub>2</sub> behaves as,
  - (a) an acid, (b) a reducing agent, (c) an oxidising agent.
  - (ii) Mention one catalyst in each case.
    - (a) Which retards H<sub>2</sub>O<sub>2</sub> decomposition.
    - (b) Which accelerates H<sub>2</sub>O<sub>2</sub> decomposition.
- 7. (i) Name the isotopes of hydrogen.
  - (ii) How many protons, neutrons and electrons are present in the isotopes of hydrogen?
  - (iii) What is the molecular mass of heavy water? Give one chemical reaction only for the preparation of deuterium from heavy water.

- (iv) Give two uses of heavy water.
- (v) Write two important uses of heavy hydrogen.
- (vi) How many different combinations of water are possible from 1H<sup>1</sup>, 1H<sup>2</sup>, 1H<sup>3</sup> and 8O<sup>16</sup>, 8O<sup>17</sup> and 8O<sup>18</sup>?
- (vii) How does heavy water react with the following?
  - (a) CaC<sub>2</sub>
- (b)  $Mg_3N_2$
- (c)  $P_2O_5$
- (d) H<sub>2</sub>SO<sub>4</sub>

#### 8. Write short notes on:

- (i) Nascent hydrogen
- (ii) Atomic hydrogen
- (iii) Ortho- and para- hydrogen
- (iv) Bosch's process
- (v) Lane's process
- (vi) Calgon
- (vii) Permutit method of softening water
- (viii) Ion-exchange method for removal of hardness of water
- (ix) Industrial applications of hydrogen
- (x) Strength of hydrogen peroxide
- (xi) Zeolite

#### 9. Explain the following:

- (i) Why are the melting and boiling points of D<sub>2</sub>O are higher than those of ordinary water?
- (ii) Presence of water is avoided in the preparation of H<sub>2</sub>O<sub>2</sub> from Na<sub>2</sub>O<sub>2</sub>.
- (iii) A mixture of hydrazine and H<sub>2</sub>O<sub>2</sub> is used as a rocketpropellant.
- (iv) Hydrogen peroxide acts as an oxidising agent as well as a reducing agent. [I.I.T. 1992]
- (v) Hydrogen peroxide gives acidic properties.
- 10. The following statements are true under certain conditions. Mention the condition in each case in a few words.
  - (i) Hydrogen reacts with oxygen to form water.
  - (ii) Hydrogen reacts with nitrogen to form ammonia.
  - (iii) Hydrogen can be prepared from water at ordinary temperatures.
  - (iv) A metal will liberate hydrogen by its reaction with dil. H<sub>2</sub>SO<sub>4</sub>.
  - (v) The unsaturated hydrocarbon, ethylene, is saturated to ethane by hydrogen.

#### Matching Type Questions

#### Match the following:

- (a) Manufacture of Hydrogen
- (b) Ionic hydride
- (c) Preparation of H<sub>2</sub>O<sub>2</sub>
- (d) Electron deficient hydride
- (e) Hard water
- (f) Heavy water
- (g) Permutit
- (h) Perhydrol

- (i) Boron hydride
- Oxide of heavy hydrogen
- (iii) Antiseptic and germicide
- (iv) An artificial zeolite
- (v) Mercks' process
- (vi) Bosch's process
- (vii) Hydrolith
- (viii) Scale in boilers

#### NUMERICAL PROBLEMS

1. What mass of CaO will be required to remove the hardness of 1000 litres of water containing 1.62 g of calcium bicarbonate per litre?

[Hint: 
$$Ca(HCO_3)_2 + CaO \longrightarrow 2CaCO_3 + H_2O + CO_2$$
]  
162 g 56 g

[Ans.  $5.6 \times 10^2$  g]

2. 100 mL of tap water containing Ca(HCO<sub>3</sub>)<sub>2</sub> was titrated with N/50 HCl with methyl orange as indicator. If 30 mL of HCl were required, calculate the temporary hardness as parts of CaCO<sub>3</sub> per 10<sup>6</sup> parts of water.

[Hint: 30 mL N/50 HCl = 30 mL N/50 Ca(HCO<sub>3</sub>)<sub>2</sub>

 $\equiv$  30 mL N/50 CaCO<sub>3</sub>  $\equiv$  100 mL tap water

Mass of CaCO<sub>3</sub> in 100 mL tap water = 
$$\frac{E \times N \times V}{1000}$$
$$= \frac{50 \times 30}{50 \times 1000} = 0.03 \text{ g}$$

[Ans. Hardness = 300 ppm]

3. 20 mL of H<sub>2</sub>O<sub>2</sub> after acidification with dilute H<sub>2</sub>SO<sub>4</sub> required 30 mL of N/12 KMnO<sub>4</sub> for complete oxidation. Calculate the percentage of H2O2 in the solution. Equivalent mass of  $H_2O_2 = 17$ .

[Hint: 30 mL 
$$\frac{N}{12}$$
 KMnO<sub>4</sub> = 20 mL  $N_x$ H<sub>2</sub>O<sub>2</sub>  
Normality of H<sub>2</sub>O<sub>2</sub> soln.,  $N_x = \frac{30}{12 \times 20} = \frac{1}{8}$   
Strength = Normality × Eq. mass =  $\frac{1}{8}$  × 17 = 2.125 gL<sup>-1</sup>  
% =  $\frac{2.125}{1000}$  × 100 = 0.2125

4. 25 mL of hydrogen peroxide solution were added to excess of acidified potassium iodide solution. The iodine so liberated required 20 mL of 0.1 N sodium thiosulphate solution. Calculate strength in terms of normality, percentage and volume.

[M.L.N.R. 1996]

[M.L.N.R. 19]
[Hint: Let the normality of 
$$H_2O_2$$
 soln. be  $N_x$ .

20 mL 0.1  $N$  Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 20% mL 0.1  $N$  I<sub>2</sub>
= 25 mL  $N_x$  H<sub>2</sub>O<sub>2</sub>

Normality of  $H_2O_2$ ,  $N_x = \frac{20 \times 0.1}{25} = \frac{2}{25} = 0.08$ 

Strength = Eq. mass × normality
= 17 × 0.08 = 1.36 gL<sup>-1</sup>

Percentage = 0.136

68 g H<sub>2</sub>O<sub>2</sub> give oxygen at NTP = 22400 mL

0.00136 g H<sub>2</sub>O<sub>2</sub> give oxygen at NTP =  $\frac{22400}{68} \times 0.00136$ 
= 0.448 mL

1 mL of H<sub>2</sub>O<sub>2</sub> solution gives 0.448 mL oxygen.]

5. What is the volume strength of a molar solution of hydrogen peroxide?

[Hint: 1 molar solution consists 34 g H<sub>2</sub>O<sub>2</sub> per litre.] [Ans. 11.2 volume]

 Calculate the mass of H<sub>2</sub>O<sub>2</sub> present in 600 mL of a 10 volume hydrogen peroxide solution.

[Ans. 18.2 g]

 10.2 g of pure H<sub>2</sub>O<sub>2</sub> are heated strongly till completely decomposed. Calculate the volume of oxygen evolved at 27°C and 740 mm pressure.

[Ans. 3792 mL]

**8.** Calculate the volume strength of a 5 N hydrogen peroxide solution.

[**Hint**: 5 N solution consists 85 g  $H_2O_2$  per litre.] [**Ans.** 28 volume]

9. There is a sample of 10 volume of hydrogen peroxide solution. Calculate its strength in (i) per cent of hydrogen peroxide and (ii) grams of H<sub>2</sub>O<sub>2</sub> per litre.

[Ans. 3.035%, 30.35 gL<sup>-1</sup>]

[M.L.N.R. 1990]

## Auswers

#### Answers: Subjective Type Questions

- 1. (a) Deuterium
  - (b) It is a mixture of CO and H<sub>2</sub>.
  - (c) LiAlH<sub>4</sub> and NaBH<sub>4</sub>.
  - (d) Elements of groups 7, 8 and 9 do not form hydrides and even the elements of group 6 except chromium do not form hydride. This region of periodic table from group 6 to 9 is termed hydride gap.
  - (e) Autoprotolysis of water means self ionisation of water.

$$H_2O + H_2O \Longrightarrow H_3O^+ + OH^-$$

- (f) The saline hydrides
- 2. (a) Water (b) Water free from all types of cations and anions is called deionised water. Yes.
  - (c) Calgon (d) (i)  $NH_3$  (ii)  $C_2H_2$  (iii)  $PH_3$
- 4. (i) No fixed position, sometimes placed in IA with alkali metals and sometimes in VIIA (or 17th) group with halogens.
  - (ii) Metals having positive oxidation potential values or placed above hydrogen in the electrochemical series evolve hydrogen with water or dilute HCl or dilute H<sub>2</sub>SO<sub>4</sub>.
  - (iii) Uyeno method,

$$2A1 + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2\uparrow$$

- (iv) Commercial zinc.
- (v) AgNO<sub>3</sub> solution.
- (vi) Either by partial oxidation or cracking.
- (vii) Ionic hydrides.
- (viii) 2800°C.
- (ix) 75.
- (x) Atomic hydrogen.
- (xi) Tritium.
- (xii) Heavy water is used as a moderator. It slows down the speed of fast neutrons.
- (xiii) The rates of reactions of D2O are slower than H2O.
- (xiv) By exhaustive electrolysis of ordinary water.
- (xv) The density of heavy hydrogen is twice that of hydrogen, hence the density of D<sub>2</sub>O is more than H<sub>2</sub>O.
- (xvi) Bicarbonates of Ca and Mg (soluble) are converted into insoluble carbonates.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

- (xvii) It is a complex salt used as water softener. It's chemical name is sodium hexametaphosphate, Na<sub>2</sub>[Na<sub>4</sub>(PO<sub>3</sub>)<sub>6</sub>].
- (xviii) p-p overlapping.
- (xix) Anthraquinone.
- (xx) CrO<sub>5</sub>, chromium peroxide,

$$K_2Cr_2O_7 + 4H_2O_2 + H_2SO_4 \xrightarrow{Ether} K_2SO_4 + 2CrO_5 + 5H_2O$$

(xxi) H2O2 gives nascent oxygen that kills bacteria.

- (xxii) 100 mL.
- (xxiii) Oxidising nature.
- (xxiv) Concentration is done by vacuum distillation.
- (xxv)  $O_3$  acts as an oxidising agent while  $H_2O_2$  acts as a reducing agent,  $H_2O_2 + O(given by O_3) \longrightarrow H_2O + O_2$ .
- 5. (a) Potassium ferricyanide is reduced.

$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 \longrightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$$

(b)  $Cr(OH)_3$  is converted into yellow coloured  $Na_2CrO_4$ .  $2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$ 

(c)  $NH_4HSO_4 \rightleftharpoons H^+ + NH_4SO_4^-$ 

At anode : 
$$2NH_4SO_4^- \longrightarrow (NH_4)_2S_2O_8 + 2e^-$$
  
Ammonium

peroxydisulphate

At cathode:  $2H^+ + 2e^- \longrightarrow H_2(g)$ (d) Hydrazine is oxidised to  $N_2$  and  $H_2O$ 

$$N_2H_4 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$$

(e) Benzene in presence of FeSO<sub>4</sub> is converted into phenol.

$$C_6H_6 + H_2O_2 \longrightarrow C_6H_5OH + H_2O$$

(f) Lactic acid is oxidised to pyruvic acid

CH<sub>3</sub>CHOHCOOH + H<sub>2</sub>O<sub>2</sub> 
$$\xrightarrow{\text{FeSO}_4}$$
 CH<sub>3</sub>COCOOH + 2H<sub>2</sub>O

(g) Tin hydride is formed.

(h) Sodium borohydride is formed.

$$B_2H_6 + 2NaH \longrightarrow 2NaBH_4$$

(i) 
$$H_2O_2 + Ba(OH)_2 \longrightarrow BaO_2 + 2H_2O$$

(j) NaOCl + 
$$H_2O_2 \longrightarrow NaCl + H_2O + O_2$$

6. (i) (a) 
$$Na_2CO_3 + H_2O_2 \longrightarrow Na_2O_2 + H_2O + CO_2$$
  
 $2NaOH + H_2O_2 \longrightarrow Na_2O_2 + 2H_2O$ 

$$O_3 + H_2O_2 \longrightarrow 2O_2 + H_2O$$

$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

(c) 
$$H_2S + H_2O_2 \longrightarrow S + 2H_2O$$

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

- (ii) The decomposition of H<sub>2</sub>O<sub>2</sub> is retarded by orthophosphoric acid while it is accelerated by presence of alkali or finely divided metals like Pt, Ag, Au, etc.
- 7. (i) Three isotopes (a) Protium (b) Deuterium (c) Tritium
- (ii) 1 proton 1 proton 1 proton
  1 electron 1 electron 1 electron
  no neutron 1 neutron 2 neutrons
  - (iii) 20; 3Fe + 4D<sub>2</sub>O  $\longrightarrow$  Fe<sub>3</sub>O<sub>4</sub> + 4D<sub>2</sub>
  - (iv) (a) As a moderator (b) for the production of deutero compounds.
  - (v) (a) For tracer studies (b) for fusion reactions.
  - (vi) 18

(b)

(vii) (a) 
$$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$$

(b) 
$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3$$

(c) 
$$P_2O_5 + 3D_2O \longrightarrow 2D_3PO_4$$

(d) 
$$H_2SO_4 + D_2O \longrightarrow D_2SO_4 + H_2O$$

- 9. (i) D<sub>2</sub>O has more molecular mass and greater degree of association than H<sub>2</sub>O and thus shows higher m.pt. and b.pt.
  - (ii) Water reacts with Na2O2 to produce NaOH which increases the decomposition of H<sub>2</sub>O<sub>2</sub>.
  - (iii) The reaction is highly exothermic. It brings large increase in volume also.

$$N_2H_4 + 2H_2O_2 \longrightarrow N_2(g) + 4H_2O(g)$$

(iv) This is due to the following reactions.

Oxidising agent:

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$
 (acidic medium)  
 $H_2O_2 + 2e^- \longrightarrow 2OH^-$  (alkaline medium)

Reducing agent:

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$$

(v) H<sub>2</sub>O<sub>2</sub> reacts with bases to form peroxides (salts) and water

$$2NaOH + H_2O_2 \longrightarrow Na_2O_2 + 2H_2O$$

$$Ba(OH)_2 + H_2O_2 \longrightarrow BaO_2 + 2H_2O$$

(i) On electrical sparking; (ii) At elevated temperature (500-550°C) and high pressure (200 atm.) in presence of a catalyst; (iii) By electrolysis or by the action of some metal like sodium in the form of amalgam; (iv) Provided the position of the metal is above hydrogen in the electrochemical series; (v) In the presence of a catalyst at elevated temperatures.

Answers: Matching Type Questions

## ILLUSTRATIONS OF OBJECTIVE QUESTIONS

- 1. An inorganic substance liberates oxygen on heating and turns an acidic solution of KI brown and reduces acidified KMnO<sub>4</sub> solution. The substance is:
  - (a) HgO

- (b) H<sub>2</sub>O<sub>2</sub>
- (c) KNO<sub>3</sub>
- (d)  $Pb(NO_3)_2$

Ans. (b)

[Hint: 
$$2H_2O_2 \xrightarrow{\text{Heat}} 2H_2O + O_2$$
;

$$2KI + H_2O_2 \xrightarrow{\text{Acidic}} 2KOH + I_2$$
;

Acidified KMnO<sub>4</sub> acts as an oxidising agent when it is decolourised,  $H_2O_2 + O \longrightarrow H_2O + O_2$ .]

- 2. The volume strength of  $10 N H_2O_2$  is :
  - (a) 112

(b) 11.2

(c) 0.112

(d) 56

Ans. (d)

**[Hint:** Volume strength =  $5.6 \times$  normality]

- 3. In which of the properties listed below, hydrogen does not show similarity with halogens?
  - I. Nature of the oxide
  - II. Electropositive character
  - III. Combination with alkali metals
  - IV. Atomicity
  - (a) I and II (b) III and IV (c) II only (d) I and III Ans. (a)

[Hint: Hydrogen forms a neutral oxide, i.e., H<sub>2</sub>O (water) while the oxides of halogens are acidic. Hydrogen shows electropositive nature also while halogens are mostly electronegative in nature.]

- In which of the following reactions does hydrogen act as an oxidising agent?
  - (a)  $H_2 + F_2 \longrightarrow$
- (b)  $H_2 + SiCl_4 \longrightarrow$
- (c) Na +  $H_2 \longrightarrow$
- (d)  $CuO + H_2 \longrightarrow$

Ans. (c)

- [Hint: The reaction in which hydrogen accepts the electron or its oxidation number changes from 0 to -1, it acts as an oxidising agent.  $2Na + H_2 \longrightarrow 2Na^+ H^-$ .]
- 5. When H<sub>2</sub>O<sub>2</sub> is added to ice cold solution of acidified potassium dichromate in ether and the contents are shaken and allowed to stand:
  - (a) a blue colour is obtained in ether due to formation of Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.
  - (b) a blue colour is obtained in ether due to formation of CrOs.
  - (c) a blue colour is obtained in ether due to formation of
  - (d) chromyl chloride is formed.

Ans. (b)

Ans. (b) [Hint: 
$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$$
]

Blue colour in ether

- 6. Mass percentage of deuterium in heavy water is:
  - (a) same as that of protium in water
  - (b) 11.1
  - (c) 20.0

(d) cannot be predicted

Ans. (c)

[Hint: The formula of heavy water is D<sub>2</sub>O, i.e., molecular mass

% of deuterium = 
$$\frac{4}{20} \times 100 = 20$$
 ]

- 7. 2 g of aluminium is treated separately with excess of dilute H<sub>2</sub>SO<sub>4</sub> and excess of NaOH. The ratio of volumes of hydrogen evolved under similar conditions of pressure and temperature
  - (a) 2:3(b) 1:1
- (c) 2:1
- (d) 1:2

Ans. (b)

[Hint: 
$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2$$
;

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$$

Thus, ratio of volumes of hydrogen evolved is 1:1]

- 8. In which reaction, hydrogen peroxide neither acts as an oxidising agent nor as a reducing agent?
  - (a) PbS +  $H_2O_2 \longrightarrow$
- (b)  $SO_3^- + H_2O_2 \longrightarrow$
- (c)  $PbO_2 + H_2O_2 \longrightarrow$
- (d)  $Na_2CO_3 + H_2O_2 \longrightarrow$

Ans. (d)

[Hint: H<sub>2</sub>O<sub>2</sub> behaves as an acid when reacts with Na<sub>2</sub>CO<sub>3</sub>.

$$Na_2CO_3 + H_2O_2 \longrightarrow Na_2O_2 + CO_2 + H_2O]$$

- 9. Which one of the following reactions does not form gaseous product?
  - (a)  $PbO_2 + H_2O_2 \longrightarrow$
- (b) PbS +  $H_2O_2 \longrightarrow$
- (c)  $Cl_2 + H_2O_2 \longrightarrow$
- (d)  $Na_2CO_3 + H_2O_2 \longrightarrow$

[Hint: PbS +  $4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$ ]

- 10. What is the degree of hardness of a sample of water containing 24 mg of MgSO<sub>4</sub> (molecular mass 120) per kg of water?
  - Ans. (c)
  - (c) 20 ppm (a) 10 ppm (b) 15 ppm

[Hint: 24 mg of MgSO<sub>4</sub> present in 10<sup>3</sup>g of water

 $10^6$ g water will contain = 24000 mg of MgSO<sub>4</sub> = 24 g of MgSO<sub>4</sub>

 $120 \text{ g of MgSO}_4 \equiv 100 \text{ g of CaCO}_3$ 

So, 24 g of MgSO<sub>4</sub> = 
$$\frac{100}{120} \times 24 = 20$$
 g of CaCO<sub>3</sub>

Hardness of water = 20 ppm]

- 11. In alkaline medium, H<sub>2</sub>O<sub>2</sub> reacts with Fe<sup>3+</sup> and Mn<sup>2+</sup>  $\label{eq:continuous} \begin{tabular}{ll} [J.E.E.~(Orissa)~2006] \\ (b)~Fe^{2+}~and~Mn^{2+} \end{tabular}$ separately to give:
  - (a) Fe<sup>4+</sup> and Mn<sup>4+</sup>
- (c) Fe<sup>2+</sup> and Mn<sup>4+</sup>
- (d) Fe<sup>4+</sup> and Mn<sup>2+</sup>

Ans. (c)

[Hint: K<sub>3</sub>Fe(CN)<sub>6</sub> is reduced by H<sub>2</sub>O<sub>2</sub> in alkaline medium.

$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 \longrightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$$

 $Mn(OH)_2$  is oxidised by  $H_2O_2$  in alkaline medium.  $Mn(OH)_2 + H_2O_2 \longrightarrow MnO_2 + 2H_2O]$ 

- 12. When a substance A reacts with water, it produces a combustible gas B and a solution of substance C in water. D reacts with this solution of C and produces the same gas B on warming. D can also produce gas B on reaction with dilute H<sub>2</sub>SO<sub>4</sub>. A imparts a deep golden yellow colour to smokeless flame. A, B, C and D respectively are:
  - (a) Na, H<sub>2</sub>, NaOH, Zn
- (b)  $K, H_2, KOH, Al$
- (c) Ca, H<sub>2</sub>, Ca(OH)<sub>2</sub>, Sn
- (d)  $CaC_2$ ,  $C_2H_2$ ,  $Ca(OH)_2$ , Fe

Ans. (a) [Hint:

- 13. Polyphosphates are used as water softening agents because they:
  - (a) form soluble complexes with anionic species
  - (b) precipitate anionic species
  - (c) form soluble complexes with cationic species
  - (d) precipitate cationic species

Ans. (c)

- 14. What is false about  $H_2O_2$ ?
  - (a) Acts both as oxidising and reducing agent
  - (b) Two OH bonds lie in the same plane
  - (c) Pale blue liquid
  - (d) Can be oxidised by O<sub>3</sub>

Ans. (b)

[Hint: Two OH bonds lie in the different planes.]



# **OBJECTIVE QUESTIONS**



**Set I:** This set contains questions with one correct answer.

1.	Hydrogen has the tendency to gain one electron to acquire	14.	Heavy water is qualified as heavy because it is:	
	helium configuration, in this respect it resembles:		(a) a heavy liquid	
	(a) alkali metals $\Box$ (b) carbon $\Box$		(b) an oxide of a heavier isotope of oxygen $\Box$	
	(c) alkaline earth metals $\Box$ (d) halogens $\Box$		(c) an oxide of deuterium $\Box$	
2.	Pure hydrogen is obtained by carrying electrolysis of:		(d) denser than water $\Box$	
	(a) water containing $H_2SO_4$	15.	Both temporary and permanent hardness in water is removed	
	(b) water containing NaOH		by:	41
	(c) Ba(OH) <sub>2</sub> solution		(a) boiling $\Box$ (b) filtration . $\Box$	ز وگ
	(d) KOH solution		(c) distillation $\Box$ (d) decantation $\Box$	٤,
3.	In Bosch's process which gas is utilised for the production	16.	Both temporary and permanent hardness is removed on	
	of hydrogen?		boiling water with:	
	(a) Producer gas $\square$ (b) Water gas $\square$		(a) $Ca(OH)_2$ $\Box$ (b) $Na_2CO_3$ $\Box$	
	(c) Coal gas	İ	(c) $CaCO_3$ $\Box$ (d) $CaO$ $\Box$	
4.	In which property listed below hydrogen does not resemble	17.	Temporary hardness is caused due to the presence of:	
	alkali metals?		(a) $CaSO_4$ $\Box$ (b) $CaCl_2$ $\Box$	
	(a) Nature of oxide		(c) $CaCO_3$	
	(b) Reducing nature	18.	Permutit is:	
	(c) Tendency to form cation		(a) hydrated sodium aluminium silicate	
	(d) Presence of one electron in valence shell		(b) sodium hexametaphosphate	
5.	Adsorbed hydrogen by palladium is known as:		(c) sodium silicate	
	(a) atomic $\Box$ (b) nascent $\Box$		(d) sodium meta-aluminate	
	(c) occluded $\Box$ (d) heavy $\Box$	19.	Calgon is an industrial name given to:	
6.	The conversion of atomic hydrogen into ordinary hydrogen		(a) normal sodium phosphate $\Box$	
	18:		(b) sodium meta-aluminate	
	(a) exothermic change $\Box$ (b) endothermic change $\Box$		(c) sodium hexametaphosphate	
	(c) nuclear change $\Box$ (d) photochemical change $\Box$		(d) hydrated sodium aluminium silicate $\Box$	
7.	The gas used in the hydrogenation of oils in presence of	20.	Which of the following is not a water softener?	
	nickel as a catalyst is:		(a) Calgon $\square$ (b) Permutit $\square$	
	(a) methane $\Box$ (b) ethane $\Box$		(c) $Na_2CO_3$ $\square$ (d) $Na_2SO_4$ $\square$	
	(c) ozone $\Box$ (d) hydrogen $\Box$	21.		
8.	The isotopes of hydrogen known is/are:		excess of sulphuric acid and excess of sodium hydroxide, the	
	(a) 4		ratio of volumes of hydrogen evolved is:	
	(c) 2 $\square$ (d) 1 $\square$		(a) 1:1 $\Box$ (b) 1:2	
9.	Tritium contains neutron/neutrons.		(c) $2:1$	
	(a) 4	22.	The temporary hardness of water due to calcium bicarbonate	:
	(c) 2		can be removed by adding:	
10.	Tritium undergoes radioactive decay giving:		(a) $CaCO_3$ $\square$ (b) $CaCl_2$ $\square$	
	(a) $\alpha$ -particles $\square$ (b) $\beta$ -particles $\square$		(c) HC1 $\Box$ (d) Ca(OH) <sub>2</sub> $\Box$	
	(c) neutrons $\Box$ (d) $\gamma$ -rays $\Box$	23.	Which elements out of the following do not produce	:
11.	The decay product of tritium is:		hydrogen on treatment with caustic soda?	
	(a) ${}_{1}^{1}H$ · $\square$ (b) ${}_{1}^{2}H$ $\square$		(i) Zn (ii) Sn (iii) Cu (iv) Ca (v) Al	
	(c) ${}_{2}^{3}\text{He}$ $\square$ (d) ${}_{2}^{4}\text{He}$ $\square$		(a) (i) and (v) $\square$ (b) (iii) and (iv) $\square$	i
12.	Deuterium differs from hydrogen in:		(c) (ii) and (iv) $\square$ (d) (iv) and (v) $\square$	
	(a) chemical properties $\Box$ (b) physical properties $\Box$	24.	7	
	(c) both physical and chemical properties		lating through it a solution of:	
	(d) radioactive properties		(a) sodium chloride	
13.	In which of the following reactions does hydrogen act as		(c) magnesium chloride	
	an oxidising agent?	25.	1.3.	
	(a) $H_2 + F_2 \longrightarrow \square$ (b) $CH_2 = CH_2 + H_2 \longrightarrow \square$		(a) $PbO_2$ $\Box$ (b) $MnO_2$ $\Box$	
	(c) PbO + H <sub>2</sub> $\longrightarrow$ $\square$ (d) Ca + H <sub>2</sub> $\longrightarrow$ $\square$	1	(c) $Na_2O_2$ $\square$ (d) $TiO_2$ $\square$	į

26.	Hydrogen gas will not reduce:			(c) reducing agent	
	(a) heated cupric oxide			(d) none of the above	
	(c) heated stannic oxide (d) heated aluminium oxide		41.	Which hydride is called alanate?	
27.	Heavy water is:			(a) $CaH_2$	
	(a) $H_2O$ $\square$ (b) $D_2O$			(c) $NaBH_4$ $\square$ (d) $AlH_3$	
	(c) water at 4°C		42.	The volume of '10 vol.' of H <sub>2</sub> O <sub>2</sub> required to liberate 500 r	mL
	(d) water obtained by repeated distillation			O <sub>2</sub> at NTP is:	
28.	The sum number of neutrons and protons in one of	the		(a) $50 \text{ mL}$	
	isotopes of hydrogen is:			(c) $100 \mathrm{mL}$ $\square$ (d) $125 \mathrm{mL}$	
	(a) 3		43.	Hydrogen peroxide has a:	
	(c) 5			(a) linear structure	
29.	A commercial sample of H <sub>2</sub> O <sub>2</sub> is labelled as '15 volume'.	Its		(b) closed chain structure	
	percentage strength is nearly:			(c) closed book type structure	
	(a) 1%			(d) half open book type structure	
	(c) 10%		44.	Hydrogen peroxide does not:	
30.	The decomposition of H <sub>2</sub> O <sub>2</sub> can be slowed down by	the		(a) liberate iodine from KI	
	addition of small amount of phosphoric acid which acts	as:		(b) turn the titanium salt yellow	
	(a) stopper			(c) give silver peroxide with moist silver oxide	
	(c) inhibitor			(d) turn the mixture of aniline, KClO <sub>3</sub> and dil. H <sub>2</sub> SO <sub>4</sub> vio	let
31.	The colour of hydrogen is:				
	(a) yellow		45.	Hydrogen peroxide was for the first time prepared by:	
	(c) red $\Box$ (d) none			(a) Priestley	
32.	Hydrogen is evolved by the action of cold dilute HNO <sub>3</sub>	on:		(c) Gay-Lussac	
	(a) Fe		46.	Hydrogen peroxide is a:	
	(c) Mg			(a) liquid	
33.	Hard water is not fit for washing clothes because:			(c) solid	
	(a) it contains Na <sub>2</sub> SO <sub>4</sub> and KCl		47.	Hydrogen peroxide is:	
	(b) it gives precipitate with soap			(a) in the form of a dilute solution	
	(c) it contains impurities			(b) in pure form	
	(d) it is acidic in nature			(c) in impure form	
34.				(d) in gaseous state	
	(a) a reducing agent		48.	When 50% solution of H <sub>2</sub> SO <sub>4</sub> is electrolysed by passin	ga
	(c) a dehydrating agent  (d) a bleaching agent			current of high density at low temperature the main produ	
35.				of electrolysis are:	
,	(a) cold dilute H <sub>2</sub> SO <sub>4</sub> on hydrated BaO <sub>2</sub>			(a) oxygen and hydrogen	
	(b) dil. HCl on MnO <sub>2</sub>			(b) H <sub>2</sub> and peroxy disulphuric acid	
	(c) cold H <sub>2</sub> SO <sub>4</sub> on MnO <sub>2</sub>			(c) H <sub>2</sub> and SO <sub>2</sub>	
	(d) aqueous alkali on Na <sub>2</sub> O <sub>2</sub>			(d) O <sub>2</sub> and peroxy disulphuric acid	
36.	Which of the following hydride is most volatile?		49.	Which one of the following reactions shows oxidis	sing
	(a) Hydrolith			nature of H <sub>2</sub> O <sub>2</sub> ?	_
	(c) Sodium hydride			(a) $H_2O_2 + 2KI \longrightarrow 2KOH + I_2$	
37.	The bleaching properties of $H_2O_2$ are due to its:			(b) $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$	
	(a) reducing properties $\square$ (b) oxidising properties			(c) $H_2O_2 + Ag_2O \longrightarrow 2Ag + H_2O + O_2$	
	(c) unstable nature			(d) NaClO + $H_2O_2 \longrightarrow NaCl + H_2O + O_2$	
38.	For the bleaching of hair, the substance used is:		50.	Ortho and Para hydrogen differ:	
	(a) $SO_2$ $\square$ (b) bleaching powder			(a) in the number of protons	
	(c) $H_2O_2$ $\square$ (d) $O_3$			(b) in the molecular mass	
39.	The reaction, $H_2S + H_2O_2 \rightarrow S + 2H_2O$ manifests:			(c) in the nature of spins of protons	
	(a) acidic nature of H <sub>2</sub> O <sub>2</sub>			(d) in the nature of spins of electrons	
	(b) alkaline nature of H <sub>2</sub> O <sub>2</sub>		51.	Decolourisation of acidified potassium permanganate occ	
	(c) oxidising action of H <sub>2</sub> O <sub>2</sub>			when $H_2O_2$ is added to it. This is due to:	
	(d) reducing nature of H <sub>2</sub> O <sub>2</sub>			(a) oxidation of KMnO <sub>4</sub>	
40.	$H_2O_2$ is:	- <del>-</del>		(b) reduction of KMnO <sub>4</sub>	
	(a) an oxidising agent			(c) both oxidation and reduction of KMnO <sub>4</sub>	
	(b) both oxidising and reducing agent			(d) none of the above	
	· · · · · · · · · · · · · · · · · · ·		1	4. A	_

52.	Which of the following metals adsorbs hydrogen?		66.	Hydrogen directly combines with:	
	(a) Zn	ן נ		(a) Ca	
	(c) Al	]		(c) Al	
53.	The permanent hardness of water can be removed by boiling	g	67.	The metal which displaces hydrogen from a boiling caus	stic
	the water with:			soda solution is:	
	(a) NaOH $\Box$ (b) Na <sub>2</sub> CO <sub>3</sub> $\Box$	]		(a) Ag	
	(c) $Na_3PO_4$	ן נ		(c) Mg	
54.	Hydrogen reacts with the following in the dark:			Hydrogen peroxide is used as:	
	(a) $Br_2$ $\square$ (b) $F_2$ $\square$			(a) oxidising agent	
	(c) $I_2$ $\square$ (d) $Cl_2$	]		(b) reducing agent	
55.	H <sub>2</sub> O <sub>2</sub> reduces K <sub>3</sub> Fe(CN) <sub>6</sub> in:	_		(c) both as oxidising and reducing agent	
	(a) neutral solution	1		(d) drying agent	
E.C	(c) alkaline medium	- 1		The melting points of most of the solid substances incre	
36.	In which of the following reactions does water act as a	n		with an increase of pressure acting on them. However,	
	oxidising agent?	<b>,</b>		melts at a temperature lower than its usual melting point when the process is in process. This is because	nen
	(a) $3F_2 + 3H_2O \longrightarrow 6HF + O_3$ (b) $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$			the pressure is increased. This is because: (a) ice is less dense than water	
	(c) $C + H_2O \longrightarrow CO + H_2$ [2] (d) $AIN + 3H_2O \longrightarrow AI(OH)_3 + NH_3$ [5]	- 1		<ul><li>(b) it generates heat</li><li>(c) chemical bonds break under pressure</li></ul>	
57	The species that do not contain peroxide ions are:	-		(d) none of the above	
٥,,	(a) $PbO_2$ $\Box$ (b) $H_2O_2$ $\Box$	٦		A mixture of hydrazine and $H_2O_2$ is:	
	(c) $SrO_2$ $\Box$ (d) $BaO_2$	1		(a) antiseptic	
58.	The 'volume strength' of $1.5 N H_2O_2$ solution is:	-		(c) germicide	
	(a) 4.8	- l		Decomposition of H <sub>2</sub> O <sub>2</sub> is accelerated by:	
	(c) 3.0	- 1		(a) traces of acids	
59.	When zeolite, which is hydrated sodium aluminium silicate	e,		(c) finely divided metals □ (d) alcohol	
	is treated with hard water the sodium ions are exchanged with	- 1	72.	The shape of water molecule is same as that of:	
	(a) $H^+$ ions $\Box$ (b) $Ca^{++}$ ions $\Box$			(a) $C_2H_2$	
	(c) $SO_4^-$ ions $\Box$ (d) $OH^-$ ions $\Box$	ן		(c) $NH_3$ $\Box$ (d) $Cl_2O$	
60.	Which of the following statements is incorrect?[BHU 2008	3]	73.	20 mL of a sample of H <sub>2</sub> O <sub>2</sub> gives 400 mL of oxyg	gen
	(a) H <sub>2</sub> O <sub>2</sub> can act as an oxidising agent	J		measured at NTP. The sample should be labelled as:	
	· · · · · · · · · · · · · · · · · · ·	<b>]</b>		(a) 5 vol. $H_2O_2$	
		]		(c) anhydrous $H_2O_2$ $\square$ (d) 20 vol. $H_2O_2$	
	(-)Z-Z FF	]	74.	An orange coloured solution acidified with H <sub>2</sub> SO <sub>4</sub> and trea	
61.	The hybrid state and oxidation state of two oxygen atoms i	n,		with a substance 'X' gives a blue coloured solution of Cr	:O <sub>5</sub> .
	$H_2O_2$ are respectively:	_ 1		The substance 'X' is:	_
		⊒		(a) $H_2O$ $\Box$ (b) dil. $HCl$	
62	(c) $sp^3$ , $-1$	]	. 75	(c) H <sub>2</sub> O <sub>2</sub>	
62.	Given colourless liquid will be determined whether it is water or not?	21	13.	Consider the two reactions:	
		<b>-</b>		$(x) H2O2 + H2S \longrightarrow S + 2H2O$	
				$(y)  H_2O_2 + O_3 \longrightarrow 2O_2 + H_2O$	
				H <sub>2</sub> O <sub>2</sub> acts as:	
		<u> </u>		(a) oxidising agent in both (x) and (y)	
63.	Heavy water is used in atomic reactor as:		٠.	(b) oxidising in (x) and reducing in (y)	
		<b>-</b>		(c) reducing in (x) and oxidising in (y)	
	(b) moderator	<b>]</b>		(d) reducing in both (x) and (y)	
	(c) both coolant and moderator	<b>-</b>	76.	Hydrogen can be placed in VIIA (or 17th group) of period	odic
	(d) neither coolant nor moderator	<b>]</b>		table because:	_
64.	Heavy water freezes at:			(a) hydrogen forms hydrides like NaH	
				(b) hydrogen has isotopes D and T	
				<ul><li>(c) it is light</li><li>(d) hydrogen combines with halogens</li></ul>	
65.	Hydrogen does not combine with:	_,	77	H <sub>2</sub> O <sub>2</sub> $\longrightarrow$ 2H <sup>+</sup> + O <sub>2</sub> + 2e <sup>-</sup> , $E^{\circ}$ = -0.68 V	ب
			, , , .	The above equation represents which of the follow	vino
	(c) Sb		ļ	behaviour of H <sub>2</sub> O <sub>2</sub> ?	·s

	(a) Reducing	l (b) Oxidising		84.	The H—O—H angle in	water	molecule is abou	ıt:
	(c) Acidic	l (d) Catalytic			*		[A	F.M.C. 2001]
78.	Which of the following is a	true structure of H <sub>2</sub> O <sub>2</sub> ?			(a) 90°		(b) 180°	
	180°	H 297°			(c) 102°		(d) 105°	
	(a) H <b>Y</b> O <b>Y</b> O—H □	] (p) \O_\(\pi\)		85.	When two ice cubes ar	e press	sed over each other	er, they unite
	ң ң	1 (d) H O=O			to form one cube. Whi	ch of t	he following force	es is respon-
	94° 94°	Н,			sible to hold them toge	ther?	[A	.F.M.C. 2001]
	(c) $0^{\frac{34}{4}}$	1 (4) >0=0			(a) Hydrogen bond for	matior	1 .	
	(8) 0 — 0	H H			(b) van der Waals' ford	ces		
79.	Hydrolysis of one mole of p	peroxydisulphuric acid prod	uces:		(c) Covalent attraction			. 🗆
	(a) two moles of sulphuric a				(d) Ionic interaction			
	(b) two moles of peroxymor			86.	The process used for the	he rem	oval of hardness	of water is:
	(c) one mole of sulphuric		roxy-		•			I.C.E.T. 2001]
	monosulphuric acid		Ó		(a) Calgon		(b) Baeyer	· , 🗖
	(d) one mole of sulphuric a	icid, one mole of peroxyme	onos-		(c) Serpeck		· · · · · · · · · · · · · · · · · · ·	
	_	nole of hydrogen peroxide		87.		ng read	ctions, H <sub>2</sub> O <sub>2</sub> acts	as a reducing
	[Hint: $H_2S_2O_8 + H_2O \longrightarrow$		```		agent?		[E.A.N	I.C.E.T. 2001]
80.	Which of the following is c				(a) $PbO_2(s) + H_2O_2(aq)$	.)——	$PbO(s) + H_2O(l)$	$+ O_2(g) \square$
	(a) It can form bonds in +1	• •	ate 🗆 -	,	(b) $Na_2SO_3(aq.) + H_2O_3$	2(aq.)	$\longrightarrow$ Na <sub>2</sub> SO <sub>4</sub> (aq.	$+ H_2O(I)$
	(b) It is collected at cathod				(c) $2KI(aq.) + H_2O_2(aq.)$			_
	(c) It has a very high ionis	•			(d) KNO <sub>2</sub> ( $aq$ .) + H <sub>2</sub> O <sub>2</sub> (			
	(d) All of the above	7.		88.				
81.	, ,	tements is correct?		00.	Action of water or dilu	te min		
	(a) Hydrogen has same ion		ı 🗆		(a) Monohydrogen		(b) Tritium	Kerala) 2002]
	(b) H has same electronega				(c) Dihydrogen		(d) Trihydrogen	
	(c) It will not be liberated a	at anode			(e) D <sub>2</sub>		(u) Timydrogen	
	(d) H has oxidation state +1	1 and -1		89	$H_2O_2$ is "5.6 volume",			
82.	Consider the following state	ements:		05.	(a) it is 1.7% weight b		me	
	I. Atomic hydrogen is	obtained by passing hydr	rogen		(b) it is $1.N$	, voiu		
	through an electric arc				(c) both is true			
	II. Hydrogen gas will not	reduce heated aluminium of	xide.		(d) none is true			ā
	III. Finely divided pallad	lium absorbs large volum	ne of	90.	H <sub>2</sub> can be obtained fro	m:		
	hydrogen gas.				(a) water gas (CO +		v liquefaction of	CO at low
	IV. Pure nascent hydrogen	is best obtained by reacting	ıg Na		temperature under			
	with $C_2H_5OH$ .				(b) water gas by oxidat			steam) which
	Which of the above statem				can be easily remo			
	·	[S.C.R.A.			(c) electrolysis of water			
	(a) I alone	( ) =			(d) all are correct			
00	(c) I, II and III	- (··)		91.	Out of the following n	netals v	which will give H	on reaction
83.	Match List I with List II and		_		with NaOH?			
	the codes given below in the		2001]		I:Zn	, II : M	Ig, III : Al, IV: Be	
	List I	List II			(a) I, II, III, IV		(b) I, III, IV	
	1. Heavy water	A. Bicarbonates of Mg	and		(c) II, IV		(d) I, III	
		Ca in water		92.	Out of LiH, MgH2 and			
	2. Temporary hard water	B. No foreign ions in v	vater		(a) all are ionic hydrid			
	3. Soft water	C. $D_2O$			(b) LiH, MgH <sub>2</sub> are ion	ic and	CuH is covalent	. 🗀
	4. Permanent hard water	D. Sulphates and chlor			(c) all are covalent			
		of Mg and Ca in wa	iter		(d) LiH is ionic, MgH <sub>2</sub>	-		
	Codes:			93.	Which of the following	g metal		
	(a) 1–C, 2–D, 3–B, 4–A				NaOH?	,		Г. (Raj.) 2003]
	(b) 1–B, 2–A, 3–C, 4–D	•			(a) Be		(b) Ba	
	(c) 1–B, 2–D, 3–C, 4–A				(c) Ca		(d) Sr	
	(d) 1–C, 2–A, 3–B, 4–D			I				

94.	Which of the following is used as rocket fuel?		(c) NaH and NH <sub>3</sub> $\square$ (d) CaH <sub>2</sub> and B <sub>2</sub> H <sub>6</sub> $\square$	1
	[P.E.T. (Raj.) 2003]	106.	b. Hydrogen is not obtained when zinc reacts with:	-
	(a) Liquid $O_2$ $\square$ (b) Liquid $N_2$ $\square$	2001	[C.E.T. (J & K) 2005	1
	(c) Liquid NH <sub>3</sub> $\square$ (d) Liquid H <sub>2</sub> $\square$		(a) steam	-
95	Water is considered to be polluted if the dissolved oxygen		(c) conc. $H_2SO_4$ $\square$ (d) dilute $HCl$ $\square$	
	(DO) content is less than ppm. [E.A.M.C.E.T. 2003]	107	7. The hardness of water sample containing 0.002 mole of mag	_
	(a) 5	107.	nesium sulphate dissolved in a litre is expressed as:	
	(a) 5		[P.E.T. (Kerala) 2007	1
96	Which of the following could act as propellant for rockets?		(a) 20 ppm	י ר
<i>J</i> 0.	[A.I.E.E. 2003]		(c) 2000 ppm	ر ا
	(a) Liquid oxygen + liquid argon		(e) 240 ppm	٠.
	(b) Liquid nitrogen + liquid oxygen		[Hint: $0.002 \text{ mol} = 240 \times 10^{-3} \text{ g} = 200 \times 10^{-3}$ ]	
	(c) Liquid hydrogen + liquid oxygen			
	(d) Liquid hydrogen + liquid oxygen		MgSO <sub>4</sub> MgSO <sub>4</sub> CaCO <sub>3</sub>	
07		108.	3. Match list I with list II. Choose the correct matching code	
91.	On burning hydrogen in air the colour of flame is:		from the choices given: [P.E.T. (Kerala) 2007	]
	[A.F.M.C. 2003]		List I List II	
	(a) green		A. BeH <sub>2</sub> L. Complex	
00	(c) yellow		B. AsH <sub>3</sub> 2. Lewis acid	
98.	Surface water contains: [A.F.M.C. 2003]		C. B <sub>2</sub> H <sub>6</sub> 3. Interstitial	
	(a) suspended impurities		D. LaH <sub>3</sub> 4. Covalent	
	(b) organic impurities		E LiAlH <sub>4</sub> 5. Intermediate	
	(c) salt	,	6. Ionic	
00	(d) salt and organic compound		(a) $A - 6$ , $B - 2$ , $C - 4$ , $D - 5$ , $E - 1$	7
99.	Water is oxidised to oxygen by: [P.E.T. (Kerala) 2003]		(b) $A - 6$ , $B - 2$ , $C - 4$ , $D - 3$ , $E - 1$	
	(a) Ozone $\Box$ (b) KMnO <sub>4</sub> $\Box$		(c) $A - 6$ , $B - 4$ , $C - 2$ , $D - 3$ , $E - 5$	
	(c) $H_2O_2$		(d) $A - 6$ , $B - 4$ , $C - 2$ , $D - 3$ , $E - 1$	
100	(e) ClO <sub>2</sub>		(e) $A - 5$ , $B - 4$ , $C - 2$ , $D - 6$ , $E - 1$	
100.	Number of H-bonds formed by a water molecule is:	109.	9. When hydrogen peroxide is added to acidified potassium	
	[M.G.I.M.S. (Wardha) 2003]	105.	dichromate, a blue colour is produced due to the formation	
	(a) 2		of: [P.E.T. (Kerala) 2007	
	(c) 1 $\square$ (d) 4 $\square$		• • • • • • • • • • • • • • • • • • • •	
101			(a) $CrO_2$ $\Box$ (b) $Cr_2O_2$ $\Box$	
101.	Water softening by Clarke's process uses:		(a) CrO <sub>3</sub> □ (b) Cr <sub>2</sub> O <sub>3</sub> □ (c) CrO <sub>ε</sub> □ (d) CrO <sup>2</sup> □	- 9
101.	Water softening by Clarke's process uses: [P.M.T. (Kerala) 2003]		(c) $CrO_5$	- 9
101.	Water softening by Clarke's process uses:  [P.M.T. (Kerala) 2003]  (a) calcium bicarbonate □	110.	(c) $\text{CrO}_5$ $\square$ (d) $\text{CrO}_4^{2^-}$ $\square$ (e) $\text{Cr}_2\text{O}_7^{2^-}$ $\square$	- 9
101.	Water softening by Clarke's process uses:  [P.M.T. (Kerala) 2003]  (a) calcium bicarbonate  (b) sodium bicarbonate	110.	(c) $\text{CrO}_5$ $\square$ (d) $\text{CrO}_4^{2-}$ $\square$ (e) $\text{Cr}_2\text{O}_7^{2-}$ $\square$ 0. The hybridization of oxygen atom in $\text{H}_2\text{O}_2$ is :	
101.	Water softening by Clarke's process uses:  [P.M.T. (Kerala) 2003]  (a) calcium bicarbonate  (b) sodium bicarbonate  (c) potash alum	110.	(c) $\text{CrO}_5$ $\square$ (d) $\text{CrO}_4^{2-}$ $\square$ (e) $\text{Cr}_2\text{O}_7^{2-}$ $\square$ 0. The hybridization of oxygen atom in $\text{H}_2\text{O}_2$ is : [P.M.T. (Kerala) 2007; C.M.C. (Vellore) 2008	· ·
101.	Water softening by Clarke's process uses:  [P.M.T. (Kerala) 2003]  (a) calcium bicarbonate (b) sodium bicarbonate (c) potash alum (d) calcium hydroxide	110.	(c) $\text{CrO}_5$ $\square$ (d) $\text{CrO}_4^{2-}$ $\square$ (e) $\text{Cr}_2\text{O}_7^{2-}$ $\square$ 0. The hybridization of oxygen atom in $\text{H}_2\text{O}_2$ is :  [P.M.T. (Kerala) 2007; C.M.C. (Vellore) 2008  (a) $sp^3d$ $\square$ (b) $sp$ $\square$	: :
	Water softening by Clarke's process uses:  [P.M.T. (Kerala) 2003]  (a) calcium bicarbonate (b) sodium bicarbonate (c) potash alum (d) calcium hydroxide (e) sodium aluminate	110.	(c) $\text{CrO}_5$ $\square$ (d) $\text{CrO}_4^{2-}$ $\square$ (e) $\text{Cr}_2\text{O}_7^{2-}$ $\square$ 0. The hybridization of oxygen atom in $\text{H}_2\text{O}_2$ is :  [P.M.T. (Kerala) 2007; C.M.C. (Vellore) 2008  (a) $sp^3d$ $\square$ (b) $sp$ $\square$	: :
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	Water softening by Clarke's process uses:  [P.M.T. (Kerala) 2003]  (a) calcium bicarbonate (b) sodium bicarbonate (c) potash alum (d) calcium hydroxide (e) sodium aluminate  The H—O—O bond angle in H <sub>2</sub> O <sub>2</sub> is: [C.E.E. (Kerala) 2004] (a) 107.28°	-	(c) $\text{CrO}_5$	5] ] ]
102.	Water softening by Clarke's process uses:  [P.M.T. (Kerala) 2003]  (a) calcium bicarbonate (b) sodium bicarbonate (c) potash alum (d) calcium hydroxide (e) sodium aluminate  The H—O—O bond angle in $H_2O_2$ is: [C.E.E. (Kerala) 2004]  (a) $107.28^\circ$	-	(c) $\text{CrO}_5$	s) :: 7]
102.	Water softening by Clarke's process uses:  [P.M.T. (Kerala) 2003]  (a) calcium bicarbonate (b) sodium bicarbonate (c) potash alum (d) calcium hydroxide (e) sodium aluminate  The H—O—O bond angle in $H_2O_2$ is: [C.E.E. (Kerala) 2004]  (a) $107.28^\circ$	-	(c) $\text{CrO}_5$	
102.	Water softening by Clarke's process uses:  [P.M.T. (Kerala) 2003]  (a) calcium bicarbonate  (b) sodium bicarbonate  (c) potash alum  (d) calcium hydroxide  (e) sodium aluminate  The H—O—O bond angle in $H_2O_2$ is: [C.E.E. (Kerala) 2004]  (a) $107.28^\circ$	111.	(c) $\text{CrO}_5$	
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102. 103.	Water softening by Clarke's process uses:  [P.M.T. (Kerala) 2003]  (a) calcium bicarbonate  (b) sodium bicarbonate  (c) potash alum  (d) calcium hydroxide  (e) sodium aluminate  The H—O—O bond angle in H <sub>2</sub> O <sub>2</sub> is: [C.E.E. (Kerala) 2004]  (a) 107.28°	111.	(c) $\text{CrO}_5$	
102. 103.	Water softening by Clarke's process uses:  [P.M.T. (Kerala) 2003]  (a) calcium bicarbonate  (b) sodium bicarbonate  (c) potash alum  (d) calcium hydroxide  (e) sodium aluminate  The H—O—O bond angle in H <sub>2</sub> O <sub>2</sub> is: [C.E.E. (Kerala) 2004]  (a) 107.28°	111.	(c) $\text{CrO}_5$	

113.	The alkali metals form salt like hydrides by direct synthesis at elevated temperatures. The thermal stability of these hydrides decreases in which of the following orders?  [C.B.S.E. 2008]		(ii) Heavy water is more associated than ordinary water. (iii) Heavy water is more effective solvent than ordinary water. Which of the above statements are correct? [C.B.S.E. 2010] (a) (i) and (ii)
	(a) $NaH > LiH > KH > RbH > CsH$		(c) (ii) and (iii) $\Box$ (d) (i) and (iii) $\Box$
	(b) $LiH > NaH > KH > RbH > CsH$	120.	The following can convert hard water into soft water:
	(c) $CsH > RbH > KH > NaH > LiH$		[C.E.C.E. (Bihar) 2010]
	(d) $KH < NaH < LiH > CsH > RbH$		(a) Sodium palmitate
114.	In context with the industrial preparation of hydrogen from		(b) $H_2O_2$
	water gas $(CO + H_2)$ which of the following is the correct		(c) Lead nitrate
	statement? [A.I.E.E.E. 2008]		$(d)^{\circ}$ Sodium aluminium silicate
	(a) CO is oxidised to CO <sub>2</sub> with steam in the presence of a	121.	$H_2O_2$ is a : [C.E.C.E. (Bihar) 2010]
	catalyst followed by absorption of $CO_2$ in alkali		(a) monobasic acid
	(b) CO and H <sub>2</sub> are fractionally separated using difference in		(c) neutral compound
	their densities	122.	Which one of the following compounds is a peroxide?
	(c) CO is removed by absorption in aqueous Cu <sub>2</sub> Cl <sub>2</sub>		[C.B.S.E. (P.M.T.) Pre. 2010]
115	(d) H <sub>2</sub> is removed through occlusion with Pd		(a) $KO_2$ $\square$ (b) $BaO_2$ $\square$
115.	The bond angle and dipole moment of water respectively are:	100	(c) $MnO_2$ $\Box$ (d) $NO_2$ $\Box$
	[J.E.E. (Orissa) 2008]	123.	Ortho and para hydrogen have: [J.E.E. (W.B.) 2010]
	(a) 109.5°, 1.84D		(a) identical chemical properties but different physical properties
116	Which one of the following is used for reviving the exhaust		properties $\square$ (b) identical physical and chemical properties $\square$
110.	permutit? [D.C.E. 2008]		(c) identical physical properties but different chemical
	(a) HCl solution $\Box$ (b) 10% CaCl <sub>2</sub> solution $\Box$		properties
	(c) $10\%$ MgCl <sub>2</sub> solution $\square$ (d) $10\%$ NaCl solution $\square$		(d) different physical and chemical properties
117.	Which of the following is not correct regarding the		(-)
	electrolytic preparation of $H_2O_2$ ? [D.C.E. 2008]	124.	$CO + H_2 \xrightarrow{300^{\circ}C/300 \text{ atm}} CH_3OH$
	(a) Lead is used as cathode		The catalyst X is: [J.E.E. (Orissa) 2010]
	(b) 50% $H_2SO_4$ is used		(a) Fe $\Box$ (b) $Cr_2O_3/ZnO$ $\Box$
	(c) Hydrogen is liberated at anode		(c) $V_2O_5$ $\square$ (d) $Al_2O_3$ $\square$
	(d) sulphuric acid undergoes oxidation	125.	Which one of the following undergoes reduction with $H_2O_2$
118.	Blackened oil painting can be restored into original form by	120.	in an alkaline medium? [P.E.T. (Kerala) 2010]
	the action of : [J.E.E. (W.B.) 2009]		(a) $Mn^{2+}$ $\Box$ (b) HOCl $\Box$
	(a) Chlorine $\Box$ (b) BaO <sub>2</sub> $\Box$		(c) PbS $\square$ (d) $Fe^{2+}$ $\square$
	(c) $H_2O_2$ $\square$ (d) $MnO_2$ $\square$		(d) $I_2$
119.	Some statements about heavy water are given below:		[Hint: $HOCl + H_2O_2 \longrightarrow HCl + H_2O + O_2$ ]
	(i) Heavy water is used as a moderator in nuclear reactors.	•	ı
Set	II: The following questions may have more than or	e corr	ect answer.
126	Which of the following metals on treatment with NaOH will	ı	(c) Sodium and ethyl alcohol
120.	liberate H <sub>2</sub> gas?		(d) Iron and steam
	(a) $Zn$ $\Box$ (b) $Sn$	130.	The oxides which give H <sub>2</sub> O <sub>2</sub> on treatment with dilute acid
	(c) Al $\Box$ (d) Mg $\Box$	100.	are:
127.	When zeolite, which is hydrated sodium aluminium silicate,		(a) $PbO_2$
	is treated with hard water, the sodium ions are exchanged		(c) $Na_2O_2$ $\square$ (d) $BaO_2$
	with:	131.	. The oxidation states of the most electronegative element in
	(a) $H_0^+$ ions $\Box$ (b) $SO_4^{2-}$ ions $\Box$		the products of the reaction between BaO <sub>2</sub> with dilute H <sub>2</sub> SO <sub>4</sub>
	(c) $C_a^{2+}$ ions $\Box$ (d) $Mg^{2+}$ ions $\Box$		are:
128.	Hydrogen will reduce:		(a) $-1$ $\square$ (b) $+1$ $\square$
	(a) heated cupric oxide $\Box$ (b) heated ferric oxide $\Box$		(c) -2
	(c) heated zinc oxide $\Box$ (d) sodium oxide $\Box$		[Hint: $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$ . The most electro-
129.	Which of the following pairs of substances on reaction will		negative element in products is oxygen. The oxidation state
	evolve H <sub>2</sub> gas?		of oxygen in $H_2O_2$ is $-1$ and in $BaSO_4$ is $-2$ .]
	(a) Iron and dilute H <sub>2</sub> SO <sub>4</sub>	132.	. In which of the following hydrides, hydrogen exists in
	(b) Copper and dilute HCl	1	negative oxidation state?

	(a) HCl	□ (b) NaH	□   13	4. Which of the followin	g heated oxides are	reduced by
	(c) CaH <sub>2</sub>	□ (d) HI		hydrogen?	, S. S. S.	
133.	An acidified solution of K	MnO <sub>4</sub> undergoes reduction v	with:	(a) $SnO_2$	$\Box$ (b) Al <sub>2</sub> O <sub>3</sub>	
	(a) H <sub>2</sub>			(c) $Fe_2O_3$	(d) CuO	
	(b) Zn/Cu couple and H <sub>2</sub> O		□ 13:	5. The reagent(s) used for	softening the tempora	ary hardness
,	(c) Na + absolute alcohol			of water is (are):		[LI.T. 2010]
	(d) $Zn/H_2SO_4$			(a) Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$\Box$ (b) Ca(OH) <sub>2</sub>	
				(c) Na <sub>2</sub> CO <sub>3</sub>	☐ (d) NaOCl	

#### Auswers 1. (d) 2. (c) **10.** (b) 3. (b) **4.** (a) 5. (c) **6.** (a) 7. (d) **8.** (b) 9. (c) 11. (c) 12. (b) **19.** (c) 13. (d) **14.** (c) 15. (c) **16.** (b) 17. (d) 18. (a) 20. (d) 21. (a) 22. (d) 24. (a) **26.** (d) **27.** (b) 28. (a) **29.** (b) **30.** (c) **23.** (a) **25.** (c) 31. (d) **32.** (c) 33. (b) **34.** (c) 35. (a) 36. (d) 37. (b) 38. (c) **39.** (c) **40.** (b) **41.** (b) **42.** (a) **43.** (d) **44.** (c) **45.** (b) **46.** (a) **47.** (a) **48.** (b) **49.** (a) **50.** (c) **51.** (b) **52.** (b) **54.** (b) **59.** (b) **60.** (d) **53.** (d) **55.** (c) **56.** (c) **57.** (a) **58.** (b) **61.** (c) **66.** (a) **69.** (a) 62. (d) **63.** (c) **64.** (b) **65.** (a) **67.** (b) **68.** (c) **70.** (b) 71. (c) 72. (d) 73. (d) 74. (c) 75. (b) **76.** (a) 77. (a) **78.** (b) **79.** (c) **80.** (d) 88. (c) **89.** (c) **90.** (d) 81. (d) **82.** (c) 83. (d) **84.** (d) 85. (a) **86.** (a) **87.** (a) **91.** (b) 92. (d) **94.** (d) 96. (c) **97.** (b) **98.** (a) 99. (d) 100. (d) **93.** (a) **95.** (a) 101. (d) 106. (c) 108. (e) 109. (c) 110. (d) 102. (d) **103.** (b) 104. (a) **105.** (a) **107.** (b) **120.** (d) 111. (b) 112. (a) 113. (b) 114. (a) 115. (c) 117. (c) 118. (c) 119. (a) **116.** (d) **121.** (b) 122. (b) 123. (a) 124. (b) 125. (b) 126. (a,b,c) 127. (c,d) **128.** (a,b,c) 129. (a,c,d) 130. (c,d) 135. (b,c) 131. (a,c) 132. (b,c) 133. (b,c,d)**134.** (a,c,d)

## **Objective Questions for IIT ASPIRANTS**



1. Hydrogen behaves as an oxidising agent in its reaction w	gen behaves a	as an	oxidising	agent m	IUS	reaction	WIU.
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- (a) chlorine
- (b) potassium
- (c) nitrogen
- □ (d) sulphur

П [Hint: An oxidising agent is a species which accepts an electron or electrons. Hydrogen accepts an electron from potassium when it forms KH

$$H_2 + 2K \longrightarrow 2KH (K^+H^-)]$$

- 2. Hydrogen cannot be obtained by:
  - (a)  $Zn + dil. H_2SO_4$
- $\Box$  (b) Zn + dil. HNO<sub>3</sub>
- (c)  $Mg + H_2O$
- $\Box$  (d) Mg + dil. H<sub>2</sub>SO<sub>4</sub>

[Hint: Zn reacts to form hydrogen with dilute HNO3. Before the hydrogen is released, it reduce HNO3 into an oxide of

- 3. Hydrogen peroxide ionises as:  $H_2O_2 \rightleftharpoons H^+ + HO_2^-$ . If pH of H<sub>2</sub>O<sub>2</sub> is 5.91 at 25°C, the ionic product of H<sub>2</sub>O<sub>2</sub> is:
  - (a)  $1.51 \times 10^{-12}$
- $\Box$  (b) 1.15 × 10<sup>-12</sup>
- (c)  $1 \times 10^{-14}$
- $\Box$  (d)  $1.1 \times 10^{-12}$

[Hint: [H<sup>+</sup>] at  $25^{\circ}$ C =  $10^{-5.91}$  =  $1.23 \times 10^{-6}$  M;  $[HO_2^-] = 1.23 \times 10^{-6} M$ 

 $K = [H^+] [HO_7^-] = [1.23 \times 10^{-6}]^2 = 1.51 \times 10^{-12}]$ 

- 4. Which of the following hydrides conducts electricity?
  - (a) SiH<sub>4</sub>
- $\Box$  (b)  $B_2H_6$
- (c) CH<sub>4</sub>
- □ (d) KH

[Hint: KH is a crystalline solid, in molten state it conducts electricity as it possesses K<sup>+</sup> and H<sup>-</sup> ions.]

- 5. The correct increasing order of the acidity of CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> is:
- 6. Hydrogen combines with other elements by:
  - (a) losing an electron
  - (b) gaining an electron
  - (c) sharing an electron
  - (d) (a), (b), (c) all are correct
- 7. Metallic hydride is formed by:
  - (a) iron
- (b) manganese
- (c) palladium
- (d) molybdenum

## tuswers

- 1. (a)
- 2. (b)
- 3. (a)
- 4. (d) **5.** (c)
- **6.** (d)
- 7. (c)

# Matrix Matching Questions for IIT Aspirants

1. Match List-II with List-II:

#### List-I

#### List-II

- (a) Hard water
- (p) Ca(HCO<sub>3</sub>)<sub>2</sub>
- (b) Temporary hardness
- (q) MgSO<sub>4</sub> (r)  $Ca^{2+}$
- (c) Sodium ion in zeolite gets
  - exchanged with
- (s)  $Mg^{2+}$
- (d) Permanent hardness Match List-I with List-II:

#### List-I

#### List-II

- (a)  $2Al + 2KOH + 2H_2O \longrightarrow$
- $2KAIO_2 + 3H_2$
- (b)  $Fe_3O_4 + 4CO \longrightarrow$
- (p) Vivification

- (q) Involved in Lane's process
- 3Fe + 4CO<sub>2</sub>

- (c)  $Fe_3O_4 + 4H_2$  3Fe + 4H<sub>2</sub>O
- (d)  $C + H_2O(g) \longrightarrow$ 
  - $CO(g) + H_2 \hat{1}$
- 3. Match List-II with List-II:

#### List-I

- (a) LiAlH<sub>4</sub>
- (b) NaBH<sub>4</sub>
- (c) CaH<sub>2</sub>

(d) LiH

- List-II
- (p) Binary hydride

(r) Uyeno's method

(s) Bosch process

- (q) Used as reducing agent for organic compounds
- (r) Complex hydride
- (s) Alanate

- 1. (a-p, q) 2. (a-r)
- (b-p)
- (c-r, s) (d-q)

(b-p, q) (c-p, q) (d-s)

- 3. (a-q, r, s) (b-q, r)
- (d-p)

## **Assertion-Reason Type Questions**

The following questions consist of two statements each, Assertion (A) and Reason (R). You are required to choose any one of the following responses for each question.

- (a) If both (A) and (R) are true and the (R) is a correct explanation of the (A).
- (b) If both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) If (A) is true but (R) is false.
- (d) If (A) is false but (R) is true.
- (e) If both (A) and (R) are false.
- 1. (A) Alkali metals form ionic hydrides.
  - (R) Alkali metals lose their valency electron which is accepted by hydrogen to form a negative ion.
- 2. (A) When blood is added to a solution of H<sub>2</sub>O<sub>2</sub>, the solution bubbles furiously.
  - (R) Catalase (an enzyme) present in blood decomposes H<sub>2</sub>O<sub>2</sub> and produces bubbles of O<sub>2</sub>.
- 3. (A) Old lead paintings regain their original colour by washing with hydrogen peroxide solution.
  - (R) Hydrogen peroxide dissolves the blackened layer by virtue of its acidic nature.

- **4.** (A) The process of adsorption of hydrogen on palladium is known as occlusion.
  - (R) The adsorbed hydrogen is more active than ordinary hydrogen.
- 5. (A) Hydrogen is prepared in the laboratory by the action of conc. H<sub>2</sub>SO<sub>4</sub> on zinc metal.
  - (R) Pure hydrogen can be obtained by the action of water on sodium hydride.
- 6. (A) Hard water is used in a nuclear reactor.
  - (R) Dilute solution of H<sub>2</sub>O<sub>2</sub> under the name of **perhydrol** is used in medicines as antiseptic for washing wounds, teeth, ears, etc.
- 7. (A) Normal hydrogen consists of a mixture of two forms: ortho (75%) and para (25%).
  - (R) Pure ortho form can be obtained at low temperature but pure para form cannot be obtained.
- 8. (A)  $H_2O_2$  is a linear molecule.
  - (R) Each oxygen is sp-hybridized.
- 9. (A) NaCl is less soluble in heavy water than in ordinary water.
  - (R) Dielectric constant of ordinary water is more than that of heavy water. [E.A.M.C.E.T. (Engg.) 2007]

# Auswers 1. (a) 2. (a) 3. (c) 4. (b) 5. (d) 6. (d) 7. (c) 8. (e) 9. (a)

## THOUGHT TYPE QUESTIONS

## THOUGHT 1

Hydrogen is thought to account for approximately 75% of the mass of the universe. Our sun and other stars, for instance, are composed mainly of hydrogen, which serves as their nuclear fuel. On earth, though hydrogen is rarely found in its uncombined state because earth's gravity is too weak to hold such light molecules. Nearly all the H<sub>2</sub> originally present in the earth's atmosphere has been lost to space. In the earth's crust and oceans, hydrogen is found in water, petroleum, proteins, carbohydrates, fats and literally millions of other compounds and is ninth most abundant element on a mass basis.

There are three isotopes of hydrogen: protium or ordinary hydrogen ( ${}^1_1H$ ); deuterium or heavy hydrogen ( ${}^2_1H$  or D) and tritium ( ${}^3_1H$  or T). The chemical properties of the three isotopes are similar because they have same electron configuration. The physical properties of three isotopes are different due to difference in their masses, *i.e.*, isotope effects.

The reaction of hydrogen and oxygen is highly exothermic, and gas mixtures that contain as little as 4% by volume hydrogen in oxygen (or in air) are highly flammable and potentially explosive.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$
  $\Delta H^\circ = -484 \text{ kJ}$ 

Hydrogen is an enormously attractive fuel because it is environmentally clean. 'Hydrogen economy' is a new field in which it is thought that our energy needs can be meet by gaseous, liquid and solid hydrogen. Since hydrogen is not a naturally occurring substance like coal, oil or natural gas, energy must be expended to produce hydrogen before it can be used. Current research therefore focuses on finding cheaper methods for extracting hydrogen.

- 1. Which fuel does produce least environmental pollution?
  - (a) Gasoline
- (b) Hydrogen
- (c) Wood
- (d) Coal
- 2. If an isotope of hydrogen has two neutrons in its atom, its atomic number and atomic mass number will respectively be:

(a) 2 and 1

(b) 3 and 1

(c) 1 and 1

- (d) 1 and 3
- 3. Which of the following gas is lightest?

  - (a) Oxygen
- (b) Nitrogen
- (c) Hydrogen
- (d) Helium
- 4. Which isotope of hydrogen is radioactive in nature?

  - (a) Protium only
- (b) Deuterium only
- (c) Deuterium and tritium
- (d) Tritium only
- 5. Abundance of H<sub>2</sub> in the earth's atmosphere is very small. This is because:
  - (a) the earth's gravity is weak to hold light molecules
  - (b) the hydrogen is inflammable
  - (c) the hydrogen readily combined with oxygen of atmosphere
  - (d) the hydrogen is diatomic in nature
- 6. Liquid H<sub>2</sub> has been used as a rocket fuel because of:
  - (a) high thrust
  - (b) its reaction with oxygen is highly exothermic
  - (c) small space it occupies
  - (d) all these are correct

## THOUGHT 2

$$\begin{bmatrix} \text{Red Hot Coke} \\ + \\ \text{Steam} \end{bmatrix} \xrightarrow[\text{Steam}]{1000^{\circ}\text{C}} \xrightarrow[\text{Steam}]{'X'} \xrightarrow[\text{Catalyst}]{500^{\circ}\text{C}} \xrightarrow[\text{Catalyst}]{'A'} + \text{H}_{2}$$

- 1. The above sequence refers to:
  - (a) Lane's process
- (b) Bosch's process
- (c) Haber's process
- (d) Ostwald's process

- 'X' is:
  - (a) water gas
- (b) producer gas
- (c) coal gas
- (d) oil gas

- 'A' is:
  - (a) carbon monoxide
- (b) oxygen
- (c) carbon dioxide
- (d) water
- 4. The catalyst 'Y' is:
  - (a)  $V_2O_5$
- (b) Ni

(c) Fe

- (d)  $Cr_2O_3 + Fe_2O_3$
- 'A' is removed by passing the gaseous mixture:
- (a) through water under high pressure of 25 atmospheres
  - (b) through acidic solution
  - (c) through alkaline solution
  - (d) through an organic solvent

#### THOUGHT 3

Hydrogen peroxide is a powerful oxidising agent. It is an electron acceptor in acidic and alkaline mediums.

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O$$

(in acidic medium)

$$H_2O_2 + 2e \longrightarrow 2OH^-$$

(in alkaline medium)

It can also act as a reducing agent towards powerful oxidising agents:

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e$$

In alkaline medium, however, its reducing nature is more effective.

$$H_2O_2 + 2OH^- \longrightarrow 2H_2O + O_2 + 2e$$

- 1. In which of the following reactions, H<sub>2</sub>O<sub>2</sub> acts as a reducing
  - (a)  $PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$
  - (b)  $Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$
  - (c)  $2KI + H_2O_2 \longrightarrow 2KOH + I_2$
  - (d)  $KNO_2 + H_2O_2 \longrightarrow KNO_3 + H_2O$
- 2. In which of the following reactions, H<sub>2</sub>O<sub>2</sub> acts as an oxidising agent?
  - (a)  $IO_4^- + H_2O_2 \longrightarrow IO_3^- + H_2O + O_2$
  - (b)  $2I^{-} + H_2O_2 + 2H^{+} \longrightarrow I_2 + 2H_2O$
  - (c)  $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$
  - (d)  $2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$
- 3. In the reaction,  $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$ ,  $H_2O_2$  acts as :
  - (a) an acid
  - (b) an oxidising agent
  - (c) a reducing agent
  - (d) both as a reducing agent and an oxidising agent

[Hint: O<sub>3</sub> acts as an oxidising agent as it gives oxygen which oxidised H2O2.

$$H_2O_2 + O \longrightarrow H_2O + O_2$$

- 4. The bleaching properties of H<sub>2</sub>O<sub>2</sub> are due to its:
  - (a) unstable nature
- (b) acidic nature
- (c) reducing nature
- (d) oxidising nature
- 5. Decolourisation of acidified KMnO<sub>4</sub> occurs when H<sub>2</sub>O<sub>2</sub> is added to it. This is due to:
  - (a) oxidation of KMnO<sub>4</sub>
  - (b) reduction of KMnO<sub>4</sub>
  - (c) both oxidation and reduction of KMnO4
  - (d) none of the above

## THOUGHT 4

On large scale, H<sub>2</sub>O<sub>2</sub> is prepared by hydrolysis of peroxydisulphuric acid obtained by electrolysis of 50% H<sub>2</sub>SO<sub>4</sub>. The strength of H<sub>2</sub>O<sub>2</sub> is expressed in number of ways namely normality, molarity, percentage strength and volume strength. Volume strength refers to the volume of O<sub>2</sub> obtained at NTP by decomposition of ImL of H<sub>2</sub>O<sub>2</sub> solution.

- 1. The volume of 20 volume H<sub>2</sub>O<sub>2</sub> solution that decolourises 200 mL of 2 N KMnO<sub>4</sub> solution in acidic medium is:
  - (a) 112mL
- (b) 336 mL
- (c) 200 mL
- (d) 224 mL

[Hint: Normality of 20 volume  $H_2O_2 = \frac{20}{5.6} N$ 

$$\therefore \frac{20}{5.6} \times V = 2 \times 200 \quad \text{or} \quad V = 112 \text{ mL} \quad ]$$

- 2. Hydrolysis of one mole of peroxydisulphuric acid gives:
  - (a) two moles of H<sub>2</sub>SO<sub>4</sub>
  - (b) two moles of Caro's acid
  - (c) one mole of H<sub>2</sub>SO<sub>4</sub> and one mole of H<sub>2</sub>SO<sub>5</sub>
  - (d) one mole of H<sub>2</sub>SO<sub>4</sub>, one mole of H<sub>2</sub>SO<sub>5</sub> and one mole of  $H_2O_2$

- 3. The volume strength of 1.5  $N H_2O_2$  solution is:
  - (a) 4.8

(b) 5.2

(c) 8.8

(d) 8.4

[Hint: Volume strength =  $5.6 \times \text{normality}$ ]

- 4. Commercial 11.2 volume H<sub>2</sub>O<sub>2</sub> solution has molarity of:
  - (a) 1.0

(c) 11.2

- (d) 1.12
- [Hint: Molarity =  $\frac{\text{Volume strength}}{110}$ ]

- What is the volume of O<sub>2</sub> liberated at NTP by complete decomposition of 100 mL of 2 M solution of H<sub>2</sub>O<sub>2</sub>?
  - (a) 22.4 L
- (b) 2.24 L
- (c) 0.224 L
- (d) 224L

[Hint: Volume strength =  $11.2 \times Molarity = 22.4$ 

$$100 \text{ mL} = 0.1 \text{ L}, i.e., 22.4 \times 0.1$$

= 
$$2.24 L O_2$$
 released ]

## uswers

	v				•	
Thought 1	<b>1.</b> (b)	<b>2.</b> (d)	3. (c)	<b>4.</b> (d)	5. (a)	<b>6.</b> (d)
Thought 2	1. (b)	2. (a)	<b>3.</b> (c)	<b>4.</b> (d)	5. (a)	
Thought 3	1. (a)	<b>2.</b> (b)	<b>3.</b> (c)	<b>4.</b> (d)	<b>5.</b> (b)	

3. (d)

**4.** (a)

## BRAIN STORMING PROBLEMS

5. (b)



- 1. What is the oxidation state of hydrogen in N<sub>3</sub>H and NH<sub>3</sub>? Indicate the nature of these compounds.
  - [Hint:N3H

Thought 4

- (Hydrogen in +1 state; acidic)
- NH<sub>3</sub>

1. (a)

- (Hydrogen in +1 state; basic)]
- 2. Write two examples of bridging hydrogens.

2. (c)

$$\begin{bmatrix} H \\ Ans. \\ H \end{bmatrix} B \begin{pmatrix} H \\ H \end{pmatrix} CO & CO \\ CO \\ H & CO \\ CO \\ CO \end{bmatrix} \leftarrow CO$$

3. Write down hydrogen bonded coordinated water in hydrates.

$$\begin{bmatrix} H & H & M & H \\ H & O - M; & O - M; \\ H & H & H \end{bmatrix} O \begin{pmatrix} M \\ M \end{pmatrix}$$

**4.** What is mass in grams of available  $O_2$  per litre from a solution of H<sub>2</sub>O<sub>2</sub>, 10 mL of which when titrated with N/20 KMnO<sub>4</sub> solution, required 25 mL for the reaction?

$$2KMnO_4 + 5H_2O_2 + 4H_2SO_4 \longrightarrow$$

$$5O_2 + 8H_2O + 2KHSO_4 + 2MnSO_4$$

[**Hint**: 
$$N_1V_1$$
 (KMnO<sub>4</sub>) =  $N_2V_2$  (H<sub>2</sub>O<sub>2</sub>)

$$\frac{1}{20} \times 25 = N_2 \times 10$$

$$N_2 = \frac{25}{200} = \frac{1}{8}$$

$$W = N \times \text{Eq. mass} = \frac{1}{8} \times 16 = 2 \text{ g}$$

5. Excess of KI and dil. H<sub>2</sub>SO<sub>4</sub> were mixed in 50 mL H<sub>2</sub>O<sub>2</sub>. The liberated I<sub>2</sub> requires 20 mL of 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Find out the strength of H<sub>2</sub>O<sub>2</sub> in g/litre.

[Hint:

$$N_1V_1$$
 (H<sub>2</sub>O<sub>2</sub>) =  $N_2V_2$  (hypo)

$$N_1 \times 50 = 0.1 \times 20$$

$$N_1 = \frac{1}{25}$$

 $N_1 = \frac{1}{25}$ g/litre strength =  $N \times \text{Eq. mass}$ 

$$=\frac{1}{25} \times 17 = 0.68$$
 g/litre]

6. What is Fenton's reagent?

[Hint: Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> used as oxidising agent or dehydrogenating agent for organic compound.]

7. In some tooth pastes hydrogen peroxide is used. What is role of  $H_2O_2$  in it?

[Ans. Hydrogen peroxide is used as antiseptic.]

8. Hydrogen peroxide acts as oxidising agent in acidic as well as basic mediums. Substantiate this fact by electrode potential data.

[Ans. 
$$H_2O_2 + 2H^+ + 2e^- = 2H_2O$$
;  $E^\circ = 1.77 \text{ V}$   
 $O_2 + 2H^+ + 2e^- = H_2O_2$ ;  $E^\circ = 0.68 \text{ V}$   
 $HO_2^- + H_2O + 2e^- = 3OH^-$ ;  $E^\circ = 0.87 \text{ V}$ ]

9. There are three samples of  $H_2O_2$  labelled as 10 vol; 15 vol; 20 vol. Half litre of each sample are mixed and then diluted with equal volume of water. Calculate volume strength of resultant solution.

[Hirat: We know,  $V = 5.6 \times N$ 

$$N_1 = \frac{10}{56}$$
;  $N_2 = \frac{15}{56}$ ,  $N_3 = \frac{20}{56}$ 

$$N_1V_1 + N_2V_2 + N_3V_3 = N_RV_R$$

$$\frac{10}{5.6} \times \frac{1}{2} + \frac{15}{5.6} \times \frac{1}{2} + \frac{20}{5.6} \times \frac{1}{2} = N_R \times 3$$

$$N_{\rm p} = 1.339$$

Volume strength =  $N_R \times 5.6 = 1.339 \times 5.6 = 7.5$ ]

- 10. Answer the following questions:
  - (a) Indicate whether ortho or para hydrogen has zero
  - (b) Indicate whether ortho or para hydrogen can be obtained in pure form.

[Ans. (a) Para hydrogen

- (b) At 0K 100% para hydrogen can be obtained.]
- 11. Predict whether H<sub>2</sub>O<sub>2</sub> acts as oxidising or reducing agent in following reactions:

(i) 
$$IO_4^- + H_2O_2 \longrightarrow IO_3^- + O_2 + H_2O$$

(ii) 
$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

(iii) 
$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

(iv) 
$$Au_2O + H_2O_2 \longrightarrow 2Au + H_2O + O_2$$

(v) 
$$2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O$$

[Ans. (i), (iii), (iv) Reducing agent; (ii), (v) Oxidising agent]

12. A 5 mL of H<sub>2</sub>O<sub>2</sub> solution liberates 0.508 g I<sub>2</sub> from an acidified KI solution. Calculate strength of H<sub>2</sub>O<sub>2</sub> solution in terms of volume strength at STP.

[Ans. 4.48]

[Hint: 
$$2KI + H_2O_2 \longrightarrow 2KOH + I_2$$
1 mole 1 mo

∴ 254 g I<sub>2</sub> is produced by 1 mole H<sub>2</sub>O<sub>2</sub>

∴ 0.508 g I<sub>2</sub> is produced by  $\frac{1}{254} \times 0.508$  mole H<sub>2</sub>O<sub>2</sub> = 2 × 10<sup>-3</sup>

$$\begin{split} \text{Molarity of } H_2O_2 &= \frac{\text{number of moles}}{\text{volume in mL}} \times 1000 \\ &= \frac{2 \times 10^{-3}}{5} \times 1000 = 0.4 \\ \text{Volume strength} &= \text{Molarity} \times 11.2 = 0.4 \times 11.2 = 4.48] \end{split}$$

13. How many types of heavy water are possible? Write down formulae of all possible heavy water molecules.

[Ans. There are six possible heavy water molecules

14. What is perhydrol? Give its composition and use.

[Ans. 30% H<sub>2</sub>O<sub>2</sub> is called perhydrol which is used as an antiseptic and germicide for washing wounds, teeth and ears.]

15. Give an example in which H<sub>2</sub>O acts as reducing agent.

[Ans. 
$$2F_2 + 2H_2O \longrightarrow O_2 + 4HF$$
  
In above reaction,  $H_2O$  acts as reducing agent.]

16. How the active hydrogen can be obtained?

[Ans. Active hydrogen can be obtained by subjecting molecular hydrogen to silent electric discharge at ordinary temperature and 0.5 mm pressure. This hydrogen has great chemical activity. The half-life period of active hydrogen is similar to that of atomic hydrogen (0.3 sec).]

- 17. Answer the following questions:
  - (i) Which of the following cannot be oxidised by H<sub>2</sub>O<sub>2</sub>?

- (ii) Hydrogen peroxide is used to wash old oil paintings. Write down the reaction involved in this process.
- (iii) H<sub>2</sub>O<sub>2</sub> on reaction with ethene gives a commercially important compound. Write down name of this compound
- (iv) Arrange CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> in decreasing order of acidic
- (v) Give the pH of D<sub>2</sub>O and H<sub>2</sub>O at 298 K.

[Ans. (i) 
$$O_3$$
 (ii) PbS +  $4H_2O_2 \rightarrow PbSO_4 + 4H_2O$ 

$$CH_2OH$$
(iii) | ; It is used as antifreeze in the radiator of car.

CH<sub>2</sub>OH (Ethylene glycol)

- (iv)  $CO_2 > H_2O_2 > H_2O$
- (v) 7.35 and 7.0]

(v) 7.35 and 7.0 ]

18. [A] + Na[Cr(OH)<sub>4</sub>] 
$$\xrightarrow{\text{H}_2\text{O}_2}$$
 [B]  $\xrightarrow{\text{H}_2\text{SO}_4}$  [C]

Yellow Orange coloured compound

What are [A], [B] and [C]? Give the reactions involved.

[Hint: 
$$2\text{NaCr}(OH)_4 + 2\text{Na}OH + 3\text{H}_2\text{O}_2 \longrightarrow 2\text{Na}_2\text{Cr}O_4 + 8\text{H}_2\text{O}$$

[A]

[B]

 $2\text{Na}_2\text{Cr}O_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}]}$ 

[B]

[C]

19. Two liquids (A) and (B) are made of same elements and are diamagnetic. Liquid (A) on treatment with KI and starch gives blue coloured solution, however, liquid (B) is neutral to litmus and does not give any response to starch iodide paper.

[Ans. 
$$(A) \rightarrow H_2O_2$$
;  $(B) \rightarrow H_2O$ ]

20. Volume strength of  $H_2O_2$  is 22.4. What volume of it is required to oxidise 3.4 g H<sub>2</sub>S gas? [Ans. 100 mL]

21. 25 mL H<sub>2</sub>O<sub>2</sub> on treatment with excess of acidified KI solution liberates iodine. Liberated iodine requires 20 mL of 0.3 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. Calculate volume strength of H<sub>2</sub>O<sub>2</sub> solution.

[Ans. 1.334]

[Hint: 
$$N_1V_1(H_2O_2) = N_2V_2(Na_2S_2O_3)$$
  
 $N_1 \times 25 = 0.3 \times 20$   
 $N_1 = 0.24$   
Volume strength of  $H_2O_2 = Normality \times 5.6$   
 $= 0.24 \times 5.6 = 1.344$ ]

22. Naturally hard water is usually preferred in drinking and soft water in working why?

[Ans. Soft water is usually acidic and contains Na<sup>+</sup> ions in place of di- and trivalent metal ions. An increased in take of Na<sup>+</sup> is known to be related to heart disease and moreover the acidic soft water is more likely to attack metallic pipes, resulting in the solution of dangerous ions such as Pb2+. One way to avoid sodium ions in drinking water and to use less soap when washing would be to drink naturally hard water and work in soft water.]

## INTEGER ANGWER INDÉGRESSIONS

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

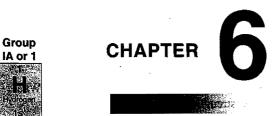
- 1. What is the sum of protons, electrons and neutrons in the heaviest isotope of hydrogen?
- 2. How much volume of 10 volume  $H_2O_2$  is required to liberate 50 cm<sup>3</sup> of oxygen at STP?
- 3. One mole of calcium phosphide on reaction with excess of water gives . . . . mole/s of phosphine.
- **4.** A commercial sample of H<sub>2</sub>O<sub>2</sub> is labelled as '10 volume'. What is its percentage strength?
- 5. What is the degree of hardness of a sample of water containing 6 mg of MgSO<sub>4</sub> (molecular mass 120) per kg of water?
- **6.** What is the molarity of a commercial sample of 33.6 volume hydrogen peroxide solution?

## Auswers

- 1. (4) In tritium atom one proton, one electron and two neutrons are present.
- 2. (5) 10 mL of  $O_2$  is obtained at STP from  $H_2O_2 = 1$  mL
- 3. (2)  $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$
- 4. (3)  $2H_2O_2 \longrightarrow 2H_2O + O_2$   $_{68 \text{ g}}$   $10 \text{ mL of oxygen is obtained from } = \frac{68}{22400} \times 10 = 0.03 \text{ g } H_2O_2$   $1 \text{ mL of } H_2O_2 \text{ solution contains } = 0.03 \text{ g } H_2O_2$

100 mL of  $H_2O_2$  solution contains = 3.0 g  $H_2O_2$ 

- 5. (5) 6 mg of MgSO<sub>4</sub> present in  $10^3$  g of water.  $10^6$  g water will contain = 6000 mg of MgSO<sub>4</sub> = 6g of MgSO<sub>4</sub> 120 g of MgSO<sub>4</sub> = 100 g of CaCO<sub>3</sub> So, 6 g of MgSO<sub>4</sub> =  $\frac{100}{120} \times 6 = 5$  g of CaCO<sub>3</sub> *i.e.*, Hardness = 5 ppm
- **6.** (3) Molarity =  $\frac{\text{Volume strength}}{11.2} = \frac{33.6}{11.2} = 3$



# Alkali Metals and their Compounds

(Group IA or  $1, ns^1$ )

#### \_\_<sub>7s'</sub>\_\_ Contents :

Lithium 2s<sup>1</sup>

Na Sodium 3s1

19

4s1 37 **Rb** Rubidium

> 5s¹ 55

Cs

Caesiur 6s1

Fr

- 6.1 Position of Alkali Metals in Periodic Table
- 6.2 Abnormal Behaviour of Lithium
- **6.2.1** Diagonal Relationship: Similarities with Magnesium
- 6.3 Lithium
- 6.4 Sodium
- 6.5 Compounds of Sodium
- 6.6 Potassium

Group	Zero	IA	IIA
Period		1	2
2	He (2)	Li (3)	Be (4)
3	Ne (10)	Na (11)	Mg (12)
4	Ar (18)	K (19)	Ca (20)
5	Kr (36)	Rb (37)	Sr (38)
6	Xe (54)	Cs (55)	Ba (56)
7	Rn (86)	Fr (87)	Ra (88)

## 6.1 POSITION OF ALKALI METALS IN PERIODIC TAB 🗵

The members of Group IA or 1, except hydrogen are called the alkali metals, because they react with water to form alkaline solutions. All the group 1A elements are soft silvery-grey metals. Their valence electron configurations are ns<sup>1</sup>, where n is the period number, and their physical and chemical properties are dominated by the ease with which the single valence electron can be removed. The group IA of the periodic table consists of six elements—lithium, sodium, potassium, rubidium, caesium and francium besides hydrogen. These elements are collectively called as alkali metals and group IA is known as alkali group as the hydroxides of these metals are soluble in water and these solutions are highly alkaline in nature. The word alkali has been derived from Arabic word 'Alquili' meaning the ashes of plants from which compounds of sodium and potassium were first isolated. They are soft enough to cut with a knife (Fig. 6.4). The alkali metals are the most reactive of all metals, reacting readily with water and air. The alkali metals, being reactive in nature, are never found free in nature but always found in combined state. The alkali metals are so reactive that, they must be stored under oil. This prevents the reaction of alkali metals with oxygen and water vapour in the air.

Of all the alkali metals, only sodium and potassium are found in abundance in nature, *i.e.*, they are seventh and eighth most abundant elements by weight in earth's crust. Their compounds are very common and have been known and used from very early times. The last member, francium, occurs only in traces as a radioactive decay product because its half life period is very small, *i.e.*, 21 minutes. Thus, not much is known about this element. The following table shows the percentage and relative abundance of alkali metals in earth's crust by weight.

Element	Percentage	Relative abundance
Li	0.0018	35
Na	2.27	7
K	1.84	8
Rb	0.0078	. 23
Cs	0.00026	46

Each alkali metal occupies a place just after a member of Zero group. Except first period, rest of the six periods of the periodic table start with a member of

alkali group. Next to the elements of Zero group, alkali metals form the most homogeneous of all the groups of the periodic table. The members of this group show a marked resemblance in their properties and possess the same electronic configuration. There is gradual gradation in the properties with the increase of atomic number. This justifies their inclusion in the same group of the periodic table. The main properties of alkali metals are discussed below for this justification.

#### 3 1. Electronic Configuration

The arrangement or the distribution of electrons on various subshells in the atoms of alkali metals is given below:

Element	At. No.		Electronic configuration	Configuration of the valency shell
Li	3	2, 1	$1s^2$ , $2s^1$	$2s^1$
Na	11	2, 8, 1	$1s^2$ , $2s^2$ $2p^6$ , $3s^1$	$3s^1$
K	19	2, 8, 8, 1	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ , $4s^1$	$4s^1$
Rb	37	2, 8, 18, 8, 1	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ , $5s^1$	$5s^1$
Cs	55	2, 8, 18, 18, 8, 1	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ , $5s^2$ $5p^6$ , $6s^1$	6s <sup>1</sup>
Fr	87	2, 8, 18, 32, 18, 8, 1	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}4f^{14}$ , $5s^2$ $5p^6$ $5d^{-1}$ , $6s^2$ $6p^6$ , $7s^1$	7s¹

The outermost shells of these elements have one electron and the penultimate (next to outermost) shells contain 8 electrons except in the first member, lithium, which contains 2 electrons, which is the atomic number of helium. Since, the last electron enters *ns*-orbital, these are called *s*-block elements.

Lithium shows somewhat abnormal properties as its electronic configuration is slightly different than the rest of the members. Because of their similarity in electronic configuration, [noble gas]  $ns^1$ , they are placed in the same sub group, *i.e.*, IA of the periodic table and closely resemble in their physical and chemical properties.

#### **2. Physical Properties**

(a) All the alkali elements are silvery white solids. These are soft in nature and can be cut with the help of knife except the lithium. When freshly cut, they have a bright lustre which quickly fades due to surface oxidation.

The silvery lustre of alkali metals is due to the presence of highly mobile electrons of the metallic lattice. There being only a single electron per atom, the metallic bonding is not so strong. As a result of this, these metals are soft in nature. However, the softness increases with increase of atomic number because there is continuous decrease of metallic bond strength on account of an increase in atomic size. Bigger is the size of metal kernel weaker is the metallic bonding.

- (b) Atomic and ionic radii: Group IA atoms are the largest in their horizontal periods in the periodic table. When the outermost electron is removed to give a positive ion, the size decreases considerably. There are two reasons for this:
- (i) The outermost shell of electron has been completely removed.
- (ii) The positive charge on the nucleus is now acting on lesser number of electrons, *i.e.*, attraction increases which brings contraction in size.

Atomic as well as ionic size increases from Li to Fr due to the presence of one extra shell of electrons.

Atomic volume also increases as the atomic number increases.

(c) Density: All are light metals. The densities are low. Lithium, sodium and potassium are lighter than water, for this very reason they float on water. Density gradually increases in moving down from Li to Cs. Potassium is, however, lighter than sodium.

The reason for the low values is that these metals have high atomic volumes. The abnormal value of potassium is due to unusual increase in atomic size, *i.e.*, atomic volume.

(d) Melting and boiling points: The energy binding the atoms in the crystal lattices of these metals is relatively low on account of a single electron in the valency shell. Consequently, the metals have low melting and boiling points. These decrease in moving down from Li to Cs as the metallic bond strength decreases or cohesive force decreases.

(e) Ionisation energies and electropositive character: Due to their large size, the outermost electron is far from the nucleus and can easily be removed. Their ionisation energies or ionisation enthalpies are relatively low. Thus, the metals have a great tendency to lose the  $ns^1$  electron to change into  $M^+$  ions. These metals are highly electropositive in nature. As the ionisation enthalpy decreases from Li to Cs, the electropositive character increases, *i.e.*, metallic character increases. The reactivity of these metals increases from Li to Cs.\*

<sup>\*(</sup>i) In gaseous state covalent molecules of  $M_2$  type are also known.

<sup>(</sup>ii) Cs metal has golden yellow appearance.

	Li	Na	K	Rb	Cs	
Ionisation enthalpy	520	496	419	403	376	
(kJ mol <sup>-1</sup> )		I	Decrease	s		
Electropositive or metallic nature	Increases					
Reactivity		1	Increase	s		

The ns<sup>1</sup> electron is so loosely held that even the low energy photons (light) can eject this electron from the metal surface. This property is termed as **photoelectric effect.** K and Cs are used in photoelectric cells which are sensitive to blue light.

(f) Oxidation states: The alkali metals can lose their  $ns^1$  electron quite easily to form univalent positive ion,  $M^+$ . The ion has a stable configuration of an inert gas.

Li <sup>+</sup>	He-configuration
Na <sup>+</sup>	Ne-configuration
K <sup>+</sup>	Ar-configuration
Rb <sup>+</sup>	Kr-configuration
Cs <sup>+</sup>	Xe-configuration

The energy required to pull out another electron from  $M^+$  ion is very high, *i.e.*, the second ionisation enthalpy values are high.

Consequently, it is not possible for alkali metals to form  $M^{2+}$  ions under ordinary conditions. These metals, thus show only one oxidation state, *i.e.*, +1 oxidation state. These metals are univalent in nature and show electrovalency, *i.e.*, form electrovalent compounds.

Since the electronic configuration of  $M^+$  ions are similar to those of inert gases, these ions have no unpaired electrons and consequently are **colourless** and **diamagnetic** in nature.

**(g) Hydration of ions, hydrated radii and hydration energy:** The salts of alkali metals are ionic and soluble in water. The solubility is due to the fact that cations get hydrated by water molecules.

$$M^+ + aq. \longrightarrow [M(aq.)]^+$$
Hydrated cation

The smaller the cation, the greater is the degree of its hydration. Thus, the degree of hydration of  $M^+$  ions decreases from  $\text{Li}^+$  to  $\text{Cs}^+$ . Consequently the radii of the hydrated ion decreases from  $\text{Li}^+$  to  $\text{Cs}^+$ .

The ionic conductance of these hydrated ions increases from  $[\text{Li}(aq.)]^+$  to  $[\text{Cs}(aq.)]^+$ .

$$[\text{Li}(aq.)]^+ < [\text{Na}(aq.)]^+ < [K(aq.)]^+ < [Rb(aq.)]^+ < [Cs(aq.)]^+$$
  
Ionic 33.5 43.5 64.5 67.5 68  
mobility at infinite dilution

Hydration of ions is an exothermic process. The energy released when one gram mole of an ion is dissolved in water to get it hydrated is called **hydration energy**. Since the degree of hydration decreases from Li<sup>+</sup> to Cs<sup>+</sup>, the hydration energy of alkali metal ion also decreases from Li<sup>+</sup> to Cs<sup>+</sup>.

Alkali metal ion  $Li^+$   $Na^+$   $K^+$   $Rb^+$   $Cs^+$  Hydration energy (kJ mol<sup>-1</sup>) -506 -406 -330 -310 -276

- **(h)** Electronegativity: The tendency to attract electrons is low as the alkali metals are electropositive. The electronegativity, thus, decreases from Li to Cs as the electropositive character increases.
- (i) Conductivity: The alkali metals are good conductors of heat and electricity. This is due to the presence of loosely held valency electrons which are free to move throughout the metal structure.
- (j) Specific heats: The specific heat values decrease from Li to Cs.

(k) Heat of atomisation: Heat of atomisation decreases from Li to Cs.

This is due to the decrease in the metallic bond strength from Li to Cs.

(I) Flame colouration: The alkali metals and their salts impart a characteristic colour to flame (Fig. 6.1).

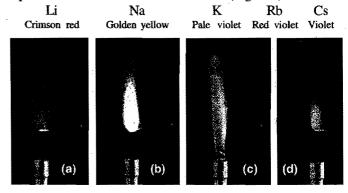


Fig. 6.1 Colour of flames of some alkali metals:
(a) Lithium (Crimson red); (b) Sodium (Golden yellow);

\_ (c) Potassium (Pale violet); (d) Rubidium (Red violet)

The reason for flame colouration is that the energy of the flame causes an excitation of the outermost electrons which on return to their original position give out the energy so absorbed in the visible region. The energy released is minimum in the case of  $Li^+$  and increases in order  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$ . Thus, the frequency of the light emitted increases in accordance with the formula E = hv. The frequency of light in lithium is minimum which corresponds to red region of the spectra.

(m) Reducing nature: An element, which acts as a reducing agent, must have low ionisation energy. Alkali metals act as strong reducing agents as their ionisation energy values are low. Since ionisation energy decreases on moving down from Li to Cs, the reducing property increases in the same

order. Thus, Li is weakest reducing agent while Cs is the strongest reducing agent amongst alkali metals in free state.

The tendency of an element to lose an electron in solution is measured by its standard oxidation potential value  $(E_{\rm ox}^{\rm o})$ . Since alkali metals have high  $E_{\rm ox}^{\rm o}$  values, these are strong reducing agents. Because their standard oxidation potentials are so strongly positive, the alkali metals can even reduce water.

$$2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq.) + \text{H}_2(g)$$

However, it is observed that Li is the strongest reducing agent amongst alkali metals in solution as  $E_{ox}^{o}$  value of Li is maximum.

It looks surprising at first sight that lithium having high value of ionisation energy amongst alkali metals acts as strongest reducing agent in solution. This can be explained if we understand the fact that ionisation energy is the property of an isolated atom in gaseous state while oxidation potential is concerned when the metal atom goes into the solution.

The ionisation energy involves the change of gaseous atom to gaseous ion,

$$M(g) \longrightarrow M^+(g) + e$$

while oxidation potential involves the following change:

$$M(s) \longrightarrow M^{+}(aq.) + e$$

The above change occurs in three steps:

(i) 
$$M(s) \longrightarrow M(g)$$
 – sublimation energy

(ii) 
$$M(g) \longrightarrow M^+(g) + e$$
-ionisation energy

(iii) 
$$M^+(g) + H_2O \longrightarrow M^+(aq) + hydration energy$$

Sublimation energy is nearly same for all the alkali metals.

The energy required in (ii) step is the ionisation energy which is highest for lithium. Li<sup>+</sup> ion is smallest in size, hence it has maximum degree of hydration. Thus, in (iii) step, maximum hydration energy is released in lithium.

·	Li	Na	. <b>K</b>
Step (i)	+122 kJ	+78 kJ	+61 kJ
Step (ii)	+520 kJ	+496 kJ	;+419 kJ
Step (iii)	- 506 kJ	– 406 kJ	-330  kJ
overall	136 kJ	168 kJ	150 kJ

Thus, with greater ease the following overall change occurs in lithium and it acts as a strongest reducing agent :

$$M(s) \longrightarrow M^+(aq.) + e$$

It is, therefore, concluded that highest reducing power of lithium in solution is due to its large heat of hydration.

#### 3. Chemical Properties

Alkali metals are highly reactive metals and the reasons for high reactivity are :

(i) They have low values of ionisation energies and readily lose their valence electron to form  $M^+$  ion.

- (ii) They have low heat of atomisation and easily come into vaporised form.
  - (iii) They have high heats of hydration.
- (a) Reactivity towards air: On exposure to moist air, all alkali metals except lithium tarnish quickly. The effect of atmosphere increases from Li to Cs. These are, therefore, always kept under kerosene to protect them from air.

$$\begin{array}{c} M \\ \text{Alkali metal} \xrightarrow{O_2} M_2\text{O} \xrightarrow{\text{H}_2\text{O}} M\text{OH} \xrightarrow{\text{CO}_2} M_2\text{CO}_3 \\ \text{Oxide} & \text{Hydroxide} \xrightarrow{\text{CO}_2} M_2\text{Co}_3 \\ \downarrow \text{O}_2 \\ M_2\text{O}_2 \\ \text{Peroxide} \end{array}$$

Lithium when heated in air combines with nitrogen to form nitride, it is due to diagonal relationship with magnesium.

All alkali metals react directly with most nonmetals (other than the noble gases). However, only lithium react with nitrogen, which it reduces to the nitride ion.

$$6\text{Li}(s) + \text{N}_2(g) \xrightarrow{\Delta} 2\text{Li}_3\text{N}(s)$$

**(b) Reactivity towards water:** Alkali metals decompose water with the evolution of hydrogen.

$$2M + 2H_2O \longrightarrow 2MOH + H_2\uparrow$$

Lithium decomposes water slowly. Sodium reacts with water quickly. K, Rb and Cs react with water vigorously. The decomposition is highly exothermic and the evolved hydrogen sometimes inflames. Thus, the reactivity towards water increases from Li to Cs. This is due to increase of electropositive character in the same order.

[The oxidation potential of lithium is highest amongst alkali metals, i.e., free energy released in the case of lithium is maximum ( $\Delta G = -nFE_{\rm ox}^{\rm o}$ ). In view of this, it looks rather surprising that lithium reacts gently with water whereas potassium which liberates less energy, reacts violently and catches fire. The explanation lies in the kinetics (the rate at which reaction proceeds) rather than in the thermodynamics (that is total amount of energy released). Potassium has a low melting point and heat of reaction is sufficient to make it melt or even vaporise. The molten metal spreads out and exposes a larger surface to the water, so it reacts even faster, gets even hotter and catches fire.]

The alkali metals also react with alcohols forming alkoxides with the evolution of hydrogen. This reaction is used in preliminary test of alcoholic group.

- (c) Affinity for non-metals: Alkali metals have great affinity for non-metals.
- (i) Reactivity towards hydrogen: The alkali metals combine directly with hydrogen to form crystalline hydrides of the formula MH. These hydrides are ionic and contain the hydride ion, H<sup>-</sup>.

$$2M + H_2 \longrightarrow 2MH$$

The electrolysis of the fused hydride (LiH) yields hydrogen at anode [other hydrides decompose before melting.] The hydrides react with water liberating hydrogen.

$$MH + H_2O \longrightarrow MOH + H_2\uparrow$$

The ionic character of the bonds in these hydrides increases from LiH to CsH and their stability decreases in the same order. They are powerful reducing agents especially at high temperatures.

$$SiCl_4 + 4NaH \longrightarrow SiH_4 + 4NaCl$$

(ii) Reactivity towards oxygen (oxides and hydroxides): Affinity towards oxygen increases. When heated in atmosphere of oxygen, the alkali metals ignite and form oxides. On combustion Li forms Li<sub>2</sub>O; sodium gives the peroxide, Na<sub>2</sub>O<sub>2</sub>; and potassium, rubidium and caesium give superoxides, MO<sub>2</sub>.

The normal oxides contain  $O_2^{-}$  ion, the peroxides contain  $O_2^{-}$  ion and superoxides contain  $O_2^{-}$  ion. The peroxides and superoxides become more stable with increase in atomic number of the alkali metal. The formation and stability of these oxides can be explained on the basis of lattice energy effects. Li<sup>+</sup> ion being a small ion has a strong positive field around it and can stabilise only a small anion,  $O_2^{-}$  whereas  $N_2^{+}$  being a large cation can stabilise a large ion and so on.

$$O^{2-}$$
  $[O-O-O]^{2-}$   $[O-O-O]^{2-}$   $[O-O-O-O]^{2-}$   $[O-O-O-O-O-O-O]^{2-}$  Superoxide

The normal oxides ' $M_2$ O' react with water to form hydroxides.

$$M_2O + H_2O \longrightarrow 2MOH$$

The basic nature of the oxides  $(M_2O)$  increases gradually on moving down in the group. The hydroxides (MOH) are colourless, strong alkaline and corrosive compounds. These are soluble in water and dissolve with the evolution of heat. The hydroxides are thermally stable except LiOH. The relative strength of the hydroxides increases from LiOH to CsOH.

The crystal structures of Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O and Rb<sub>2</sub>O are antifluorite structures. Cs<sub>2</sub>O has an anti-CdCl<sub>2</sub> layer structure.

The higher oxides, *viz.*, peroxides and superoxides are strong oxidising agents. They react with dilute acids forming hydrogen peroxide and oxygen respectively.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$
  
 $4KO_2 + 2H_2SO_4 \longrightarrow 2K_2SO_4 + 2H_2O + 3O_2$   
 $2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$ 

The peroxides are diamagnetic in nature (all the electrons are paired) and are regarded as the salts of the dibasic acid,  $H_2O_2$ . The superoxides are paramagnetic and coloured as odd

electron bond is present between two oxygen atoms. Yellow colour of Na<sub>2</sub>O<sub>2</sub> is probably due to the presence of small amount of superoxide. Superoxides are even stronger oxidising agents than peroxides.

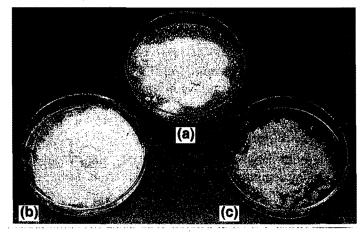


Fig. 6.2 When alkali metals react with oxygen gives different colour oxides: (a) lithium gives light colour oxides (b) sodium gives very pale yellow peroxide and (c) potassium gives yellow coloured superoxide

(iii) Reactivity towards halogens: The alkali metals directly react with halogens forming the halides of the type MX.

$$2M + X_2 \longrightarrow 2MX$$

The reactivity of alkali metals towards a particular halogen increases from Li to Cs. On the other hand, reactivity of halogens towards a particular alkali metal decreases from  $F_2$  to  $I_2$  *i.e.*,

$$F_2 > Cl_2 > Br_2 > I_2$$

With the exception of certain lithium halides, the alkali metal halides are ionic compounds  $(M^+X^-)$ . The halides are crystalline and have high melting and boiling points. The fused halides are good conductors of electricity and are used for the preparation of alkali metals. All halides except LiF dissolve in water.

Alkali metal halides are colourless but on heating they turn yellow, blue, etc., owing to non-stoichiometry and crystal defects.

Halides of potassium, rubidium and caesium have a property of combining with extra halogen atoms forming polyhalides.

$$KI + I_2 \longrightarrow KI_3$$

[The insolubility of LiF in water can be explained in the following manner. The lithium ion has the highest energy of hydration as it is small in size in comparison to other alkali metal ions and thus it should have high solubility. However, the small Li<sup>+</sup> and F<sup>-</sup> ions interact very strongly resulting in high lattice energy of LiF which is responsible for its insolubility (the ionic compounds, which possess low value of lattice energy, are freely soluble in water).]

(iv) Action with sulphur and phosphorus: Alkali metals directly combine with sulphur and phosphorus when heated with them. The monosulphides,  $M_2S$ , cannot be obtained by

passing H<sub>2</sub>S through their salt solutions as sulphides get hydrolysed.

$$M_2S + H_2O \implies MOH + MHS$$

Phosphides on hydrolysis evolve phosphine.

$$3M + P \longrightarrow M_3P$$
  
 $M_3P + 3H_2O \longrightarrow 3MOH + PH_3$ 

- (d) Nature of oxysalts: Alkali metals readily react with oxyacids forming corresponding salts with evolution of hydrogen. Lithium salts behave abnormally due to polarising power of Li<sup>+</sup>ion (small size) and lattice energy effects. However, the salts of rest of the alkali metals behave similarly and there is a gradual gradation in their properties with the increase of atomic number.
- (i) Nature of carbonates and bicarbonates: All the alkali metals form carbonates of the type  $M_2\text{CO}_3$ . Since the alkali metals are highly electropositive, their carbonates are highly stable towards heat and readily soluble in water. As the electropositive character increases from Li to Cs, the stability of the carbonates increases in the same order.

$$Cs_2CO_3 > Rb_2CO_3 > K_2CO_3 > Na_2CO_3 > Li_2CO_3$$

Li<sub>2</sub>CO<sub>3</sub> decomposes on heating and is insoluble in water. The aqueous solutions of carbonates are alkaline. This is due to hydrolysis as carbonates are salts of strong bases and weak acid (H<sub>2</sub>CO<sub>3</sub> carbonic acid).

$$M_2\text{CO}_3 + 2\text{H}_2\text{O} \Longrightarrow 2M\text{OH} + \text{H}_2\text{CO}_3$$
  
Strong alkali Weak acid

The bicarbonates, MHCO<sub>3</sub>, of the alkali metals, with the exception of lithium, are known in solid state. The bicarbonates are soluble in water. On heating, bicarbonates decompose into carbonates with evolution of CO<sub>2</sub>.

$$2MHCO_3 \longrightarrow M_2CO_3 + H_2O + CO_2$$

The abnormal behaviour of Li<sub>2</sub>CO<sub>3</sub> towards heat can be explained in the following manner.

The Li<sup>+</sup> ion exerts a strong polarising action and distorts the electron cloud of the nearby oxygen atom of the large CO<sub>3</sub><sup>2</sup> ion. This results in the weakening of the C—O bond and strengthening of the Li—O bond. This ultimately facilitates the decomposition of Li<sub>2</sub>CO<sub>3</sub> into Li<sub>2</sub>O and CO<sub>2</sub>. The lattice energy of Li<sub>2</sub>O is higher than the lattice energy of carbonate. This also favours the decomposition of Li<sub>2</sub>CO<sub>3</sub>.

Lithium due to its less electropositive nature, does not form solid bicarbonate.

(ii) Nature of nitrates: Nitrates of the type, MNO<sub>3</sub>, are known. These are colourless, soluble in water and electrovalent in nature. The nitrates do not undergo hydrolysis. With the exception of LiNO<sub>3</sub>, the other nitrates decompose to nitrites and oxygen.

$$2MNO_3 \longrightarrow 2MNO_2 + O_2$$

Lithium nitrate decompose to oxide on heating, it is due to diagonal relationship with magnesium.

$$2\text{LiNO}_3 \longrightarrow \text{Li}_2\text{O} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$$

(iii) Nature of sulphates: Sulphates of the type  $M_2SO_4$  are known. With the exception of  $Li_2SO_4$ , other sulphates are soluble in water. The sulphates when fused with carbon form sulphides.

$$M_2SO_4 + 4C \longrightarrow M_2S + 4CO$$

The sulphates of alkali metals form double salts with the sulphates of the trivalent metals like Fe, Al, Cr, etc. The double sulphates crystallise with large number of water molecules as potash alum,  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$  consists of 24 water molecules. Sulphate of lithium is not known to form alum.

(iv) Nature of perchlorates: Perchlorates of the type  $MClO_4$  are known. The stability increases gradually as larger  $M^+$  ion form more stable lattice with large  $ClO_4^-$  ion. The solubility of perchlorates decreases.

$$LiClO_4 > NaClO_4 > KClO_4 > RbClO_4 > CSClO_4$$

LiClO<sub>4</sub> is ten times more soluble than NaClO<sub>4</sub>. It is mainly due to extensive solvation of smaller Li<sup>+</sup>.

(e) Solubility in liquid ammonia: The alkali metals dissolve in liquid ammonia without the evolution of hydrogen. The colour of the dilute solutions is blue. The metal atom loses electron and it combines with ammonia molecule.

$$M \longrightarrow M^+$$
 (in liquid ammonia) + e (ammoniated)  
 $M + (x + y)NH_3 \longrightarrow [M(NH_3)_x]^+ + e (NH_3)_y$   
Solvated electron

On heating its blue colour changes to bronze.

It is ammoniated electron which is responsible for colour. The solutions are good conductors of electricity and have strong reducing properties. The solutions are paramagnetic in nature.

When dry ammonia is passed over hot metal, amides are formed.

$$2M + 2NH_3 \longrightarrow 2MNH_2 + H_2 \uparrow$$
Amide

The amides are decomposed by cold water with evolution of  $NH_3$ .

$$MNH_2 + H_2O \longrightarrow MOH + NH_3$$

Recent studies proved the existence of Li(NH<sub>3</sub>)<sub>4</sub>, a golden yellow solid.

- (f) Formation of alloys: The alkali metals form alloys amongst themselves and with other metals. These combine with mercury readily forming amalgams.
- (g) Complex formation: Alkali metals have a very little tendency to form complexes. Lithium being small in size forms certain complexes but this tendency decreases as the size increases.
- (i) Extraction of alkali metals: Alkali metals cannot be extracted by the application of common processes used for the extraction of metals due to following reasons:
- (i) Alkali metals are strong reducing agents, hence cannot be extracted by reduction of their oxides and other compounds.
- (ii) Being highly electropositive in nature, it is not possible to apply the method of displacing them from their salt solutions by any other element.

(iii) The aqueous solutions of their salts cannot be used for extraction by electrolytic method because hydrogen is discharged at cathode instead of an alkali metal as the discharge potentials of alkali metals are high. However, by using Hg as cathode, alkali metal can be deposited. The alkali metal readily combines with Hg to form an amalgam from which its recovery is very difficult.

The only successful method, therefore, is the electrolysis of their fused salts, usually chlorides. Generally, another metal chloride is added to lower its fusion temperature.

### 6.2 ABNORMAL BEHAVIOUR OF LITHIUM

The lithium, being the first member of alkali group, exhibits the characteristic properties of alkali metals but it differs at the same time in many respects from them. Reasons for its abnormal behaviour are mainly due to the following reasons:

- (i) Lithium atom and its ion has very small size. Lithium ion (Li<sup>+</sup>) on account of its small size exerts high polarising effect on anions in its compounds resulting in increased covalent character.
- (ii) Lithium atom has highest ionisation enthalpy and low electropositive character as compared to other alkali metals.
  - (iii) Nonavailability of *d*-orbitals in its valence shell.
- (iv) Lithium has strong metallic bonding which is responsible for its low reactivity to some extent.

## Lithium differs from alkali metals in the following respects:

- (i) It is more harder and lighter than other alkali metals.
- (ii) It is not affected by air easily and does not lose its lustre even on melting.
  - (iii) It reacts slowly with water to liberate hydrogen.
- (iv) It does not react with oxygen below 0°C. When burnt in air or oxygen, it forms only monoxide, Li<sub>2</sub>O. However, the rest of the alkali metals give peroxides or superoxides. Li<sub>2</sub>O is much less basic than oxides of other alkali metals.
- (v) Lithium is the only alkali metal which directly reacts with nitrogen to form Li<sub>3</sub>N.
- (vi) Lithium hydroxide decomposes at red heat to form Li<sub>2</sub>O. Hydroxides of other alkali metals donot decompose.

$$2\text{LiOH} \longrightarrow \text{Li}_2\text{O} + \text{H}_2\text{O}$$

- (vii) Lithium bicarbonate, LiHCO<sub>3</sub> is known in solution but not in solid state while the bicarbonates of other alkali metals are known in solid state.
  - (viii) Li<sub>2</sub>CO<sub>3</sub> is less stable, as it decomposes on heating.

$$\text{Li}_2\text{CO}_3 \longrightarrow \text{Li}_2\text{O} + \text{CO}_2$$

The other carbonates are stable.

(ix) LiNO<sub>3</sub>, on heating gives a mixture of  $NO_2$  and  $O_2$  while nitrates of rest of alkali metals yield only oxygen.

$$4\text{LiNO}_3 \longrightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$$
  
 $2\text{NaNO}_3 \longrightarrow 2\text{NaNO}_2 + \text{O}_2$ 

(x) Li<sub>2</sub>SO<sub>4</sub> is the only alkali metal sulphate which does not form double salts, *e.g.*, alums.

- (xi) Lithium reacts with bromine very slowly. Other alkali metals react violently.
- (xii) Lithium fluoride (LiF), lithium phosphate (Li<sub>3</sub>PO<sub>4</sub>), lithium oxalate (Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>), etc., are sparingly soluble in water. The corresponding salts of other alkali metals are freely soluble in water.
- (xiii) LiCl is highly deliquescent and soluble in alcohol and pyridine. LiCl separates out from aqueous solution as hydrated crystals LiCl·2H<sub>2</sub>O whereas chlorides of other alkali metals are insoluble in organic solvents and do not form hydrated crystals under ordinary temperatures.
- (xiv) Li when heated in  $NH_3$  forms imide  $Li_2NH$  while other alkali metals form amides,  $MNH_2$ .
  - (xv) LiOH is much weaker base than NaOH or KOH.

# DIAGONAL RELATIONSHIP : SIMILARITIES WITH MAGNESIUM

Lithium shows resemblance with magnesium, an element of group IIA. This resemblance is termed as **diagonal relationship**.



#### Reasons for the diagonal relationship are the following:

- (i) Electronegativities of Li and Mg are quite comparable. (Li = 1.00, Mg = 1.20)
- (ii) Atomic radii and ionic radii of Li and Mg are not very much different.

(iii) Atomic volumes of Li and Mg are quite similar.

(iv) Both have high polarising power (ionic potential)

Polarising power 
$$(\Phi) = \frac{\text{Ionic charge}}{(\text{Ionic radius})^2}$$

Cations with large ionic potentials have a tendency to polarise the anions and to give partial covalent character to compounds.

Lithium resembles magnesium in the following respects:

- (a) Both Li and Mg are harder and have higher melting points than the other metals in their respective groups.
  - (b) Li like Mg decomposes water slowly to liberate hydrogen.

$$2\text{Li} + 2\text{H}_2\text{O} \longrightarrow 2\text{LiOH} + \text{H}_2$$
  
 $\text{Mg} + 2\text{H}_2\text{O} \longrightarrow \text{Mg(OH)}_2 + \text{H}_2$ 

(c) Both the elements combine with nitrogen on heating.

$$\begin{array}{ccc} 6\text{Li} & + & N_2 & \longrightarrow & 2\text{Li}_3N \\ 3\text{Mg} & + & N_2 & \longrightarrow & \text{Mg}_3N_2 \end{array}$$

Both the nitrides are decomposed by water with evolution of ammonia (NH<sub>3</sub>).

$$\text{Li}_3\text{N} + 3\text{H}_2\text{O} \longrightarrow 3\text{LiOH} + \text{NH}_3$$
  
 $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$ 

(d) Both Li and Mg combine with carbon on heating.

$$2Li + 2C \longrightarrow Li_2C_2$$

$$Mg + 2C \longrightarrow MgC_2$$

Both the carbides yield C<sub>2</sub>H<sub>2</sub> with water.

(e) Lithium forms only monoxide when heated in oxygen. Mg also forms the monoxide.

$$4Li + O_2 \longrightarrow 2Li_2O$$
  
 $2Mg + O_2 \longrightarrow 2MgO$ 

Both the oxides are less soluble in water.

(f) Hydroxides of Li and Mg are weak bases and are slightly soluble in water. Both decompose on heating.

- (g) Lithium fluoride, phosphate, oxalate and carbonate, like the corresponding salts of Mg, are sparingly soluble in water.
  - (h) Carbonates of Li and Mg decompose on heating.

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$
  
 $MgCO_3 \longrightarrow MgO + CO_2$ 

(i) Nitrates of Li and Mg decompose on heating giving mixture of nitrogen dioxide and oxygen.

$$4\text{LiNO}_3 \longrightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$$
  
 $2\text{Mg(NO}_3)_2 \longrightarrow 2\text{MgO} + 4\text{NO}_2 + \text{O}_2$ 

- (j) Chlorides of both Li and Mg are deliquescent and soluble in alcohol and pyridine. Lithium chloride like magnesium chloride, (MgCl<sub>2</sub>·6H<sub>2</sub>O) separates out from solutions as hydrated crystals, LiCl·2H<sub>2</sub>O.
- (k) Li<sub>2</sub>SO<sub>4</sub> like MgSO<sub>4</sub> does not form double sulphates, *i.e.*, alums.
- (l) The bicarbonates of Li and Mg do not exist in solid state, they exist in solutions only.
  - (m) Lithium salts like magnesium salts undergo hydrolysis.
  - (n) Alkyls of Li and Mg are soluble in organic solvents.

#### **Example 1.** Explain the following:

- (a) The softness of group IA metals increases down the group with increasing atomic number. [HT 1986]
- (b) Lithium salts have a greater degree of covalent character than other halides of the group.
- (c) Li<sup>+</sup> ion is far smaller than the other alkali metal ions but it moves through a solution less rapidly than the others.
- (d) Lithium fluoride has the lowest solubility of the group IA metal halides.
- (e) Salts of lithium having small anions are more stable than the salts having larger anions.

**Solution:** (a) The metallic bond strength is low in the case of alkali metals as only one electron per large sized metal

atom is available. Thus, alkali metals are soft in nature. However, the size of the metal ion increases with increasing atomic number, the metallic bond strength decreases and, therefore, softness increases.

- (b) The small size of Li<sup>+</sup> gives it a huge polarising power. The electron cloud of larger halide ion gets distorted and this leads to covalency.
- (c) The dense charge of Li<sup>+</sup> attracts several layers of water molecules around it, *i.e.*, Li<sup>+</sup> has maximum degree of hydration. Thus, the size of the hydrated lithium ion is largest in comparison to the size of the other hydrated metal ions which affects its movement in solution.
- (d) The small size of both the Li<sup>+</sup> and F<sup>-</sup> ions leads to a very large lattice energy and thus, the crystal is very hard to break apart.
- (e) The salts of Li<sup>+</sup> with small anions have high lattice energy and thus very stable while with large anion, the lattice energy decreases and the salts become less stable.

#### **Example 2.** Explain the following:

- (a) Alkali metals do not occur free in nature.
- (b) Alkali metals are good reducing agents.
- (c) Alkali metal salts impart colour to the flame.

[Roorkee 1986]

- (d) Sodium is kept under kerosene.
- (e) Potassium and caesium are used in photoelectric cells.

**Solution:** (a) Since the ionisation potential values of alkali metals are low, they are very reactive in nature. They readily combine with oxygen, moisture and  $CO_2$  of the atmosphere and many other substances. Hence, they do not occur free in nature.

- (b) Alkali metals act as strong reducing agents because they can lose valency electrons easily on account of low ionisation potential values and high values of oxidation potentials.
- (c) The energy of the flame causes an excitation of the outermost electron which on return to its original position gives out energy so absorbed in the visible region. The amount of energy released increases from Li<sup>+</sup> to Cs<sup>+</sup>. Thus, the frequency of light emitted increases in accordance with the formula E = hv. The frequency of light is minimum in lithium which corresponds to red light.
- (d) Sodium is highly electropositive and hence is very reactive. It readily combines with oxygen, moisture and CO<sub>2</sub> of the atmosphere. Hence, it is always kept in kerosene as to prevent the action of atmosphere.
- (e) Because of low ionisation potentials, potassium and caesium are used in photoelectric cells. The low energy photons (light) can eject electrons from their metal surface.

#### 6.3 LITHIUM

**Occurrence:** Lithium is rare but is widely distributed in the earth's crust. Its amount present in any mineral is generally

low and, thus, its extraction is somewhat difficult. Important minerals of lithium are:

- (a) Aluminosilicates: These include the following minerals.
- (i) Lepidolite or lithiamica, (Li, Na, K)<sub>2</sub>·Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub>(F, OH)<sub>2</sub>. It contains 2-6% lithium.
  - (ii) Spodumene, LiAl(SiO<sub>3</sub>)<sub>2</sub>. It contains 3.8 to 5.6% lithium.
  - (iii) Petalite, LiAl(Si<sub>2</sub>O<sub>5</sub>)<sub>2</sub>. It contains 2 to 3% lithium.
  - (b) Phosphates: These include the following minerals:
- (i) Triphylite, (Li, Na)<sub>3</sub>PO<sub>4</sub> (Fe, Mn)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. It is a double phosphate and contains about 1.5 to 3.5% lithium.
- (ii) Amblygonite, Li(AlF)PO<sub>4</sub>. It contains 7 to 10% lithium. Lithium occurs in traces in soils, sea water, certain spring waters, blood, muscular tissues and ashes of some plants such as sugar cane, beat, tobacco, coffee, etc.

Lithium occurs in India mainly as lepidolite in Bihar, Kashmir, Karnataka and Rajasthan.

**Extraction:** The extraction of lithium from any one of the minerals involves two steps:

- (i) Preparation of lithium chloride from the mineral.
- (ii) Electrolysis of lithium chloride.

#### (i) Preparation of Lithium Chloride, LiCI

(a) From lepidolite: The powdered mineral is fused with a mixture of barium carbonate, barium sulphate and potassium sulphate. In fused state, two layers are separated. The upper layer contains sulphates of lithium, sodium and potassium while the lower layer contains heavier materials such as silicates, barium sulphate, aluminium sulphate, alumina, silica, etc.

The upper layer is dissolved in minimum quantity of water and then the solution is treated with barium chloride. The sulphates of Li, Na and K react and form corresponding soluble chlorides and insoluble barium sulphate with barium chloride.

$$\text{Li}_2\text{SO}_4 + \text{BaCl}_2 \longrightarrow 2\text{LiCl} + \text{BaSO}_4$$
  
 $\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \longrightarrow 2\text{NaCl} + \text{BaSO}_4$   
 $\text{K}_2\text{SO}_4 + \text{BaCl}_2 \longrightarrow 2\text{KCl} + \text{BaSO}_4$ 

The insoluble barium sulphate is removed by filtration. The solution containing chlorides of Li, Na and K is evaporated to dryness. LiCl is extracted from the solid residue with the help of pyridine. LiCl dissolves in pyridine while other chlorides remain insoluble. From the pyridine solution, LiCl is recovered by distillation.

(b) From triphylite ore (phosphate ore): The powdered ore is digested with conc. HCl. H<sub>3</sub>PO<sub>4</sub> comes into the solution along with chlorides of Li, Na, Mn and Fe. The phosphate is removed from the solution in the same manner as it is done in qualitative analysis. The solution is neutralised with NH<sub>4</sub>OH and then a buffer solution containing CH<sub>3</sub>COOH and CH<sub>3</sub>COONa is added. Now neutral FeCl<sub>3</sub> solution is added when FePO<sub>4</sub> gets precipitated. It is filtered off.

$$H_3PO_4 + FeCl_3 \longrightarrow FePO_4 + 3HCl$$

The filtrate is evaporated to dryness and the solid residue is extracted with hot water. Mn is removed as MnS by the addition of BaS.

$$MnCl_2 + BaS \longrightarrow MnS + BaCl_2$$

 $MnCl_2 + BaS \longrightarrow MnS + BaCl_2$ The filtrate is now treated with  $H_2SO_4$  to remove barium as barium sulphate.

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$$
  
 $BaS + H_2SO_4 \longrightarrow BaSO_4 + H_2S$ 

The filtrate containing Li<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> is evaporated with oxalic acid. The oxalates of lithium and sodium formed, on ignition give corresponding carbonates.

$$Li_2SO_4 + H_2C_2O_4 \longrightarrow Li_2C_2O_4 + H_2SO_4$$

$$Li_2C_2O_4 \longrightarrow Li_2CO_3 + CO$$

$$Na_2C_2O_4 \longrightarrow Na_2CO_3 + CO$$

The carbonates on treatment with HCl give their chlorides. LiCl is extracted from the mixture with pyridine.

#### (ii) Electrolysis of LiCl

Lithium is obtained by the electrolysis of a fused mixture of lithium chloride and potassium chloride in equal amounts. The addition of potassium chloride serves the following purposes:

- (i) It increases the conductivity of the fused mass.
- (ii) It lowers the fusion temperature of lithium chloride.

The electrolysis is carried out in a steel vessel with refractory lining inside. The cell is fitted with a graphite anode and a steel cathode which is surrounded by cast iron enclosure so that lithium and chlorine formed during electrolysis may not come in contact with each other (Fig. 6.3).

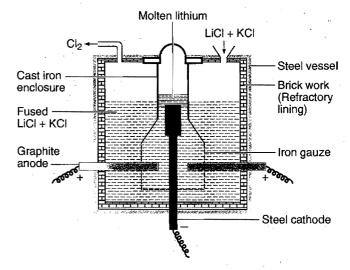


Fig. 6.3 Electrolysis of lithium chloride

The cell is operated at a voltage of 8-9 volt at 400-450°C temperature. When electric current is passed, lithium ions, in preference to potassium ions, get discharged at cathode while chloride ions are discharged at anode.

At cathode,  $Li^+ + e \longrightarrow Li$ 

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

The molten lithium containing about 1.3% of potassium, being lighter, rises to the surface of the fused electrolyte in the cast iron enclosure. The metal is removed intermittently and stored either in well stoppered bottles or in liquids like ether, petrol, etc.

#### **■** Properties

**Physical:** (i) It is a silvery white metal. It is harder than sodium and potassium. It has two naturally occurring isotopes <sup>6</sup>Li and <sup>7</sup>Li. <sup>7</sup>Li is most stable isotope. <sup>6</sup>Li is used as tritium source in thermonuclear reactions.

$${}_{3}^{6}\text{Li} + {}_{0}^{1}n \longrightarrow {}_{1}^{3}\text{H} + {}_{2}^{4}\text{He}$$

- (ii) It is very light. It's density is 0.534 at 20°C which is the lowest of all metals.
- (iii) It melts at 180.5°C. When volatilized it imparts red colour to flame. Its boiling point is 1347°C.
- (iv) It is a good conductor of heat and electricity. It has the highest specific heat (0.96).
- (v) It forms an amalgam and alloys with a number of other metals. An alloy of composition, Li = 1.1%, Cu = 4.5%, Mn=0.5%, Cd=0.2% and rest Al is used in aircraft construction.

**Chemical:** (i) Reactivity towards air: Lithium is not affected by dry air but is oxidised when moisture is present. When heated in air above 180°C, it burns with brilliant light forming lithium oxide and lithium nitride.

$$4\text{Li} + \text{O}_2 \longrightarrow 2\text{Li}_2\text{O}$$
 (Lithium oxide)  
 $6\text{Li} + \text{N}_2 \longrightarrow 2\text{Li}_3\text{N}$  (Lithium nitride)

(ii) Reactivity towards water: Lithium reacts with water forming lithium hydroxide and liberating hydrogen. However, the reaction is not vigorous due to high melting point.

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2\uparrow$$

- (iii) The oxidation potential of lithium is high, i.e., + 3.04 volt. Thus, it acts as a strong reducing agent in solution.
- (iv) Reactivity towards non-metals: Lithium combines with a number of non-metals and form stable compounds. The reaction usually occurs when lithium is heated above its fusion point. These compounds are ionic in nature and their stability is due to the fact that a small lithium cation is held by a small anion.

$$\begin{array}{lll} 2 \text{Li} + \text{H}_2 & \longrightarrow 2 \text{LiH} \\ 6 \text{Li} + \text{N}_2 & \longrightarrow 2 \text{Li}_3 \text{N} \\ 4 \text{Li} + \text{O}_2 & \longrightarrow 2 \text{Li}_2 \text{O} \\ 2 \text{Li} + \text{S} & \longrightarrow \text{Li}_2 \text{S} \\ 3 \text{Li} + \text{P} & \longrightarrow \text{Li}_3 \text{P} \\ 2 \text{Li} + 2 \text{C} & \longrightarrow \text{Li}_2 \text{C}_2 \\ 2 \text{Li} + X_2 & \longrightarrow 2 \text{LiX} \end{array} \end{aligned} \begin{tabular}{ll} \text{(Lithium hydride)} \\ \text{(Lithium oxide)} \\ \text{(Lithium sulphide)} \\ \text{(Lithium phosphide)} \\ \text{(Lithium carbide)} \\ \text{(Lithium halide)} \\ \text{(Lithium halide)} \\ \text{(X = F, Cl, Br or I)} \\ \end{tabular}$$

Except LiF, all other halides show somewhat covalent nature as the small Li<sup>+</sup> cation brings more and more polarisation (distortion) in the molecule as the size of the halide ion,  $X^-$ , increases.

(v) Reactivity towards acids: Lithium, being strongly electropositive, reacts with dilute and conc. HCl and dilute  $H_2SO_4$  (non-oxidising acids) liberating hydrogen.

$$2\text{Li} + 2\text{HCl} \longrightarrow 2\text{LiCl} + \text{H}_2 \uparrow$$
  
 $2\text{Li} + \text{H}_2 \text{SO}_4 \longrightarrow \text{Li}_2 \text{SO}_4 + \text{H}_2 \uparrow$ 

However, the reaction with conc. H<sub>2</sub>SO<sub>4</sub> is slow. HNO<sub>3</sub> attacks lithium violently. The metal melts and catches fire.

$$2\text{Li} + 2\text{HNO}_3 \longrightarrow 2\text{LiNO}_3 + \text{H}_2 \uparrow$$

The oxy-salts are not stable towards heat and decompose on heating forming stable monoxide, Li<sub>2</sub>O.

$$2\text{LinO}_3 \longrightarrow \text{Li}_2\text{O} + 2\text{NO}_2 + \left(\frac{1}{2}\right)\text{O}_2$$
  
 $\text{Li}_2\text{CO}_3 \longrightarrow \text{Li}_2\text{O} + \text{CO}_2$ 

- (vi) Reactivity towards alkalies: Alkalies have no action on lithium.
- (vii) Reactivity towards ammonia: Lithium reacts with ammonia when passed over hot metal to yield H<sub>2</sub>.

$$\begin{array}{ccc} 2Li + NH_{3} & \longrightarrow & Li_{2}NH & + H_{2} \\ & & & \text{(Lithium imide)} \end{array}$$

However, lithium dissolves in liquid ammonia and forms blue coloured solution.

(viii) Lithium forms a number of alkyls and aryls. These compounds are formed from the alkyl or aryl halides, usually the chloride, in the solvent such as ether, cyclohexane or toluene.

$$RCI + 2Li \longrightarrow LiR + LiCI$$

These compounds are usually tetrameric,  $(LiCH_3)_4$ , or hexameric,  $(LiC_2H_5)_6$ . These lithium alkyls or aryls are used in the preparation of organometallic and organic compounds.

$$\begin{array}{c} \text{Li}R + \text{CO}_2 \longrightarrow R \text{COOH} + \text{LiOH} & \text{(carboxylic acids)} \\ \text{Li}R + \text{Cl}_2 \longrightarrow R \text{--Cl} + \text{LiCl} & \text{(alkyl/aryl halide)} \\ 2\text{Li}R + 3\text{CO} \longrightarrow R_2 \text{CO} + 2\text{LiCO} & \text{(ketones)} \\ 3\text{Li}R + \text{BCl}_3 \longrightarrow \text{B}R_3 + 3\text{LiCl} & \text{(organoboron compound)} \\ 4\text{Li}R + \text{SnCl}_4 \longrightarrow \text{Sn}R_4 + 4\text{LiCl} & \text{(organotin compound)} \\ 2\text{Li}R + \text{HgI}_2 \longrightarrow \text{Hg}R_2 + 2\text{LiI} & \text{(organomercury compound)} \\ \end{array}$$

#### Uses

- (i) In the refining of metals: Lithium is used as deoxidiser in the purification of nickel and copper. It removes the last traces of oxygen and nitrogen.
- (ii) In the preparation of useful alloys: Lithium is used in the manufacture of a number of alloys. It increases tensile strength and resistance to corrosion.
- (a) Lead-lithium alloy is used for making bearings for motor engines.

- (b) Aluminium-lithium alloy is used to make aircraft parts which are light and strong.
  - (c) Magnesium-lithium alloy is used to make armour-plate.
- (iii) Thermonuclear purposes: There is a great interest in lithium for thermonuclear purposes, since when bombarded with neutrons, it produces tritium.

$${}_{3}^{6}\text{Li} + {}_{0}^{1}n \longrightarrow {}_{1}^{3}\text{H} + {}_{2}^{4}\text{He}$$

$${}_{3}^{7}\text{Li} + {}_{0}^{1}n \longrightarrow {}_{1}^{3}\text{H} + {}_{2}^{4}\text{He} + {}_{0}^{1}n$$

It is also used in the production of thermonuclear energy required for propelling rockets and missiles.

- (iv) Lithium batteries: Lithium batteries are used wherever a reliable current is required for a lengthy period. Pacemaker battery is a type of lithium battery. Lithium is used to make both primary and secondary batteries. Primary batteries have Li-anodes, carbon cathodes and SOCl<sub>2</sub> as an electrolyte. It is strongly favoured to replace the lead-acid battery for electric vehicle propulsion.
  - (v) Lithium compounds have a number of applications:
- (a) Lithium hydroxide is used in the production of lithium soaps, which are used in making lubricating greases from oil (lithium soap thickens the oil). More than 60 per cent of all automotive greases contain lithium. The compound used is lithium stearate, C<sub>17</sub>H<sub>35</sub>COOLi, which is mixed with oil to give a water resistant grease-like material that does not harden at cold temperatures and also stable at high temperatures.
- (b) Lithium aluminium hydride, LiAlH<sub>4</sub>, is used as a reducing agent in organic chemistry.
- (c) Lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>), which is obtained from lithium ore, is the primary source of other lithium compounds. Lithium carbonate is also used in the preparation of special type of glass. It increases the strength and resistance of glass. Significant quantities of lithium carbonate are also used in the preparation of porcelain, enamels and glazes.
  - (d) Lithium chloride is used in air-conditioning plants.
- (e) Lithium bicarbonate, lithium salicylate, lithium acetyl salicylate, etc., are used in medicines.
- (f) Lithium alkyls/aryls are used in the preparation of organometallic compounds. Butyllithium, LiC<sub>4</sub>H<sub>9</sub>, is a useful reagent in organic chemistry.
- (g) Lithium compounds have been used in the synthesis of vitamin-A and some pharmaceuticals.
- (h) Lithium salts are used in ceramics to prevent surface cracking of pottery.
- (i) Lithium hydroxide is used to remove carbon dioxide from air in spacecraft and submarine.

#### 6.4 SODIUM

Sodium is soft, silvery-grey, most abundant alkali metal. It can be cut easily with a sharp knife (Fig. 6.4). It forms 2.27% of the earth's crust. It was isolated by Sir Humphry Davy in 1807 by the electrolysis of fused caustic soda. Being reactive, it is

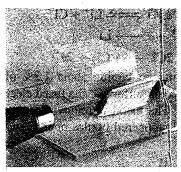


Fig. 6.4 Elemental sodium is a soft metal that can be cut easily with a knife.

never found free in nature. The most important compound of sodium found in nature is the common salt (NaCl). It is also known as lake salt, rock salt, sea salt, common salt or table salt. Sea water contains 2.0–2.9% sodium chloride. Sodium metal as well as other sodium compounds are produced from sodium chloride. Other important compounds of sodium found in nature are:

- (i) Chile saltpetre, NaNO3
- (ii) Glauber's salt, Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O
- (iii) Trona, Na<sub>2</sub>CO<sub>3</sub>·2NaHCO<sub>3</sub>·3H<sub>2</sub>O
- (iv) Natron, Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O
- (v) Tincal (Borax), Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O
- (vi) Cryolite, Na<sub>3</sub>AlF<sub>6</sub>
- (vii) Soda feldspar, NaAlSi<sub>3</sub>O<sub>8</sub>

#### **■** Preparation

Sodium is obtained on large scale by two processes:

- (i) Castner's process
- (ii) Down's process
- (i) Castner's process: In this process, electrolysis of fused sodium hydroxide is carried out at 330°C using iron as cathode and nickel as anode.

$$2\text{NaOH} \implies 2\text{Na}^+ + 2\text{OH}^-$$

At cathode:  $2Na^+ + 2e \longrightarrow 2Na$ 

At anode: 
$$4OH^- \longrightarrow 2H_2O + O_2 + 4e$$

During electrolysis, oxygen and water are produced. Water formed at the anode gets partly evaporated and is partly broken down and hydrogen is discharged at cathode.

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode:  $2H^+ + 2e \longrightarrow 2H \longrightarrow H_2 \uparrow$ 

(ii) Down's cocess: Now-a-days sodium metal is manufactured by this process. It involves the electrolysis of fused sodium chloride containing calcium chloride and potassium fluoride using iron as cathode and graphite as anode at about 600°C, the melting point of the mixture.

Sodium chloride, obtained from rock salt or sea water, is mixed with calcium chloride and melted. The calcium chloride is added to the sodium chloride electrolyte to reduce the working temperature of the cell from 801°C (the melting point of sodium chloride) to 600°C (the melting point of the mixture). This saves electrical energy and, therefore, makes the process more economical.

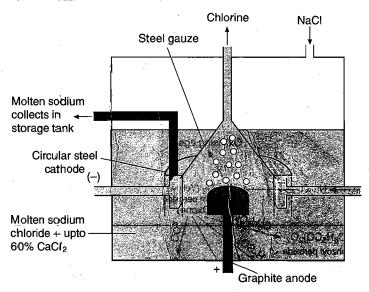


Fig. 6.5 The Down's cell used for the electrolysis of sodium chloride

The cathode is a circle of steel around the graphite anode. At 600°C sodium and chlorine would react violently together to re-form sodium chloride. To prevent this from happening, the Down's cell contains a steel gauze around the graphite anode to keep it and the cathode apart. The molten sodium float on the electrolyte and is run off for storage. A problem arises, however, is that the calcium ions are also attracted to the cathode, where they form calcium metal. Therefore, the sodium which is run off contains a significant amount of calcium. Fortunately, the calcium crystallises out when the mixture cools and relatively pure sodium metal remains.

The worldwide production of sodium metal each year is about 60,000 to 80,000 tonnes.

The overall reaction which takes place in the cell is,

$$NaCl \rightleftharpoons Na^+ + ^1Cl^-$$

At cathode:  $Na^+ + e \longrightarrow Na$ 

At anode:  $2Cl^- \longrightarrow Cl_2 + 2e$ 

The electrolysis of pure NaCl presents the following difficulties:

- (a) The fusion temperature of NaCl is high, *i.e.*, 801°C. At this temperature both sodium and chlorine are corrosive.
  - (b) Sodium forms a metallic fog at this temperature.

To remove above difficulties, the fusion temperature is reduced from 801°C to 600°C by adding CaCl<sub>2</sub> and KF. This is a cheaper method and chlorine is obtained as a byproduct.

#### Properties

**Physi il Properties:** (a) It is a silvery white metal when freshly cut but the surface is readily tarnished on exposure. The most stable isotope of sodium is  $^{23}_{11}$ Na. Many radioactive isotopes of sodium such as  $^{20}_{11}$ Na,  $^{21}_{11}$ Na,  $^{22}_{11}$ Na,  $^{24}_{11}$ Na,  $^{25}_{11}$ Na are known. Among these  $^{24}_{11}$ Na has shortest half life (0.02 seconds).

- (b) It is soft in nature and lighter than water.
- (c) It is malleable and ductile in nature.
- (d) It is good conductor of heat and electricity.
- (e) It has low melting point. It melts at a temperature of only 371 K or 97.8°C (Just below the normal boiling point of water) and its boiling point is 1156 K.
  - (f) With mercury, it forms an amalgam.
- (g) It dissolves in liquid ammonia forming intense blue coloured solution.
- (h) It gives two bright lines  $D_1$  (589.2 nm) and  $D_2$  (590.4 nm) in the yellow region of spectrum.

**Chemical Properties:** (a) Reactivity towards air: On keeping it in the moist atmosphere, it loses its lustre on account of the formation of oxide, hydroxide and carbonate.

$$4Na + O_2 \longrightarrow 2Na_2O \xrightarrow{2H_2O} 4NaOH \xrightarrow{2CO_2} In atmosphere$$

$$2Na_2CO_3 + 2H_2O$$

It is always, therefore, kept under kerosene because it corrodes rapidly by reacting with water vapour in the air. On heating in air or oxygen, it forms a mixture of Na<sub>2</sub>O and Na<sub>2</sub>O<sub>2</sub>. Na<sub>2</sub>O<sub>2</sub> is industrially known as **oxone**.

$$\begin{array}{c} 4Na \ + \ O_2 \longrightarrow \ 2Na_2O \\ 4Na \ + \ 2O_2 \longrightarrow \ 2Na_2O_2 \\ \text{Sodium peroxide} \end{array}$$

The peroxide ion,  $O_2^{2-}$  acts as an oxidizing agent.

**(b) Reactivity towards water:** It decomposes water vigorously with evolution of heat and liberating hydrogen. Sometimes the hydrogen catches fire.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

(c) Reactivity towards acids: It is strongly electropositive in nature, easily loses electron and converted into monovalent ion, Na<sup>+</sup>. On account of this, it readily displaces hydrogen from acids and forms corresponding salts.

$$2Na + 2HCl \longrightarrow 2NaCl + H_2$$

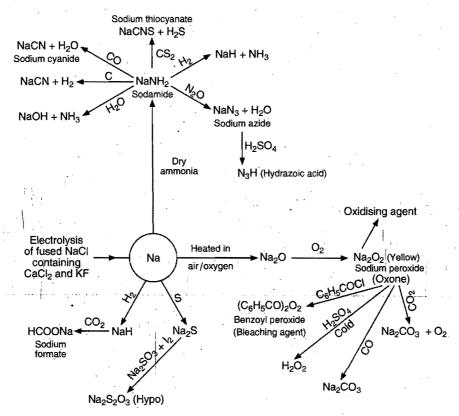
(d) Affinity for non-metals: It has high affinity for non-metals. Except carbon and nitrogen, it directly reacts with hydrogen, halogens, sulphur, phosphorus, etc., to form corresponding compounds on heating.

$$2Na + H_2 \xrightarrow{300^{\circ}C} 2NaH$$

$$2Na + Cl_2 \longrightarrow 2NaCl$$

$$2Na + S \longrightarrow Na_2S$$

$$3Na + P \longrightarrow Na_3P$$



Flowsheet diagram of properties of sodium and preparation of some important compounds

**(e) Reducing agent:** On account of low value of ionisation potential and high value of oxidation potential, it acts as a strong reducing agent.

$$SiO_2 + 4Na \longrightarrow Si + 2Na_2O$$
  
 $3CO_2 + 4Na \longrightarrow C + 2Na_2CO_3$   
 $Al_2O_3 + 6Na \longrightarrow 2Al + 3Na_2O$   
 $BeCl_2 + 2Na \longrightarrow Be + 2NaCl$ 

(f) Reactivity towards ammonia: When dry ammonia is passed over sodium at 300–400°C in absence of air, sodamide is formed with liberation of hydrogen.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2$$

Sodamide is a waxy solid and is used for making a number of sodium compounds.

#### Uses

Sodium is used:

- (i) in the manufacture of various chemicals like sodium peroxide (Na<sub>2</sub>O<sub>2</sub>), sodamide (NaNH<sub>2</sub>), sodium cyanide (NaCN), etc.
- (ii) for making lead tetraethyl (used as antiknock in petrol).

$$4C_2H_5Cl + 4Na-Pb \longrightarrow (C_2H_5)_4Pb + 3Pb + 4NaCl$$

(iii) in the preparation of sodium amalgam (used as a reducing agent).

- (iv) in molten state in nuclear reactors as heat transfer medium.
  - (v) in sodium vapour lamps which emit yellow light.
  - (vi) as a laboratory reagent for organic analysis.
- (vii) in high temperature thermometers in the form of sodium potassium alloy.
  - (viii) for the extraction of C, Be, Mg and Si.
- (ix) largely as a reducing agent in industry for the production of artificial rubber, dyes, pharmaceutical drugs, etc.
- (x) for filling exhaust valves of aeroplane engines on account of its lightness and high thermal conductivity.
  - (xi) as a liquid coolant in nuclear power stations.
- (xii) molten sodium metal is used to produce zirconium and titanium from their chloride.

$$TiCl_4(g) + 4Na \xrightarrow{\Delta} 4NaCl(s) + Ti(s)$$

## COMPOUNDS OF SODIUM

#### ■ 1. Sodium Oxide, Na<sub>2</sub>O

**Preparation:** It is prepared by heating sodium nitrate or sodium nitrite with sodium.

$$2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2$$
  
 $2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$ 

Pure sodium oxide is formed when the mixture of sodium azide and sodium nitrite is heated.

$$3NaN_3 + NaNO_2 \longrightarrow 2Na_2O + 5N_2$$

**Properties:** It is a white amorphous substance. It reacts with water violently forming sodium hydroxide and evolving a large amount of heat energy.

$$Na_2O + H_2O \longrightarrow 2NaOH + Heat$$

On heating at 400°C, it disproportionates forming sodium peroxide and metallic sodium vapour.

$$2Na_2O \xrightarrow{400^{\circ}C} Na_2O_2 + 2Na$$

Sodamide is formed when it reacts with liquid ammonia.

$$Na_2O + NH_3 \longrightarrow NaNH_2 + NaOH$$

**Uses:** It is used as dehydrating and polymerising agent in organic chemistry.

#### ■ 2. Sodium Peroxide, Na<sub>2</sub>O<sub>2</sub>

**Preparation:** It is formed by heating sodium in excess of air free from moisture and carbon dioxide or in excess of pure oxygen.

$$2Na + O_2(excess) \xrightarrow{350^{\circ}C} Na_2O_2$$

**Properties:** It is a pale yellow powder. On exposure, it becomes white as it reacts with moisture and carbon dioxide.

$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$$

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$

At low temperature, it forms H<sub>2</sub>O<sub>2</sub> with water and acids.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

It combines with CO and CO<sub>2</sub>.

$$Na_2O_2 + CO \longrightarrow Na_2CO_3$$

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$

It acts as a powerful oxidising agent.

(a) Chromic compounds are oxidised to chromates.

$$[Na_2O_2 + H_2O \longrightarrow 2NaOH + O] \times 3$$

$$2Cr(OH)_3 + 4NaOH + 3O \longrightarrow 2Na_2CrO_4 + 5H_2O$$

$$2Cr(OH)_3 + 3Na_2O_2 \longrightarrow 2Na_2CrO_4 + 2NaOH + 2H_2O$$

(b) Manganous salt is oxidised to sodium manganate.

$$[Na_2O_2 + H_2O \longrightarrow 2NaOH + O] \times 2$$

$$MnSO_4 + 4NaOH + 2O \longrightarrow Na_2MnO_4 + Na_2SO_4 + 2H_2O$$

$$MnSO_4 + 2Na_2O_2 \longrightarrow Na_2MnO_4 + Na_2SO_4$$

(c) Sulphides are oxidised to corresponding sulphates.

$$Na_2S + 4O \longrightarrow Na_2SO_4$$

Benzoyl peroxide (bleaching agent) is formed when  $C_6H_5COCl$  reacts with  $Na_2O_2$ .

$$2C_6H_5COC1 + Na_2O_2 \longrightarrow (C_6H_5CO)_2O_2 + 2NaC1$$
Benzoyl peroxide

**Uses:** It is used:

- (i) as an oxidising agent in laboratory.
- (ii) for the production of oxygen under the name oxone.
- (iii) for the purification of air.
- (iv) as a bleaching agent for delicate fibres like wool, silk, etc.
  - (v) for the preparation of benzoyl peroxide.
  - (vi) for the preparation of  $H_2O_2$ .

#### 3. Sodium Hydroxide (Caustic Soda), NaOH

Sodium hydroxide, NaOH, is a soft, waxy, white, corrosive solid. It is commonly known as lye or caustic soda. It is one of the important chemicals and is manufactured on a very large scale forming an important chemical industry. It is most conveniently manufactured by one of the following processes:

# (a) Methods involving sodium carbonate as a starting material

Two methods are used. These are:

(i) Causticisation process (Gossage process): This process depends on the reaction between suspension of lime (milk of lime, calcium hydroxide) and sodium carbonate. This reaction is reversible.

$$Na_2CO_3 + Ca(OH)_2 \Longrightarrow CaCO_3 + 2NaOH$$

Calcium carbonate being only slightly soluble separates out as a mud. The temperature is maintained 80–90°C by blowing steam. Caustic soda solution is drained out and evaporated to dryness when flakes of caustic soda are obtained.

The most suitable concentration of sodium carbonate taken in this process is 15–20%. The caustic soda produced by this method is not pure and contains some calcium carbonate, sodium carbonate and calcium hydroxide as impurities.

(ii) Lowig's process: In this process, a mixture of sodium carbonate and ferric oxide is heated to redness in a revolving furnace. Sodium ferrite is thus formed with evolution of carbon dioxide.

The sodium ferrite is cooled and thrown into hot water. The hydrolysis of sodium ferrite occurs forming a solution of sodium hydroxide and insoluble ferric oxide (Fe<sub>2</sub>O<sub>3</sub>).

$$2NaFeO_2 + H_2O \longrightarrow 2NaOH + Fe_2O_3$$

The solution is filtered and evaporated to dryness to get flakes of sodium hydroxide.

#### (b) Methods involving sodium chloride as starting material

Methods used are electrolytic as the electrolysis of sodium chloride solution is carried out in an electrolytic cell. **Principle:** A sodium chloride solution contains Na<sup>+</sup>, H<sup>+</sup>, Cl<sup>-</sup> and OH<sup>-</sup> ions.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
  
 $H_2O \rightleftharpoons H^+ + OH^-$ 

On passing electricity, Na<sup>+</sup> and H<sup>+</sup> ions move towards cathode and Cl<sup>-</sup> and OH<sup>-</sup> ions move towards anode. The discharge potential of H<sup>+</sup> ions is less than Na<sup>+</sup> ions, thus hydrogen ions get discharged easily and hydrogen is liberated. Similarly, at anode Cl<sup>-</sup> ions are easily discharged as their discharge potential is less than that of OH<sup>-</sup> ions. Cl<sub>2</sub> gas is, therefore, liberated at anode.

The solution on electrolysis becomes richer in Na<sup>+</sup> and OH<sup>-</sup> ions.

Since, chlorine reacts with sodium hydroxide solution even in the cold forming sodium chloride and sodium hypochlorite, it is necessary that chlorine should not come in contact with sodium hydroxide during electrolysis.

$$2NaOH + Cl_2 \longrightarrow NaCl + NaClO + H_2O$$

To overcome this problem, the anode is separated from the cathode in the electrolytic cell either by using a porous diaphragm or by using a mercury cathode.

Four methods are used, these are:

- (i) Porous diaphragm process (Nelson cell process)
- (ii) Castner-Kellner cell
- (iii) Solvay-Kellner cell
- (iv) Diaphragm cell
- (i) Porous diaphragm process (Nelson cell process): Nelson cell consists of a perforated steel tube

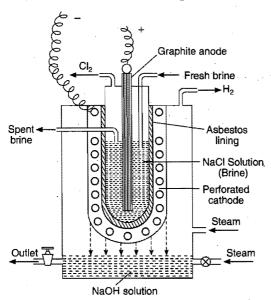


Fig. 6.6 Nelson cell

lined inside with asbestos. The tube acts as a cathode (Fig. 6.6).

It is suspended in a steel tank. A graphite rod dipped in sodium chloride solution serves as anode. On passing electric current,

chlorine is liberated at the anode and let out through the outlet. Sodium ions penetrate through the asbestos and reach the cathode where hydrogen and OH<sup>-</sup> ions are formed by reduction of water. Sodium ions combine with OH<sup>-</sup> ions to form NaOH which is collected in the outer tank while hydrogen is drawn off through the outlet. The steam blown during the process keeps the electrolyte warm and helps to keep perforation clear.

NaCl 
$$\rightleftharpoons$$
 Na<sup>+</sup> + Cl<sup>-</sup> (in solution)  
At cathode:  $2H_2O + 2e \rightleftharpoons H_2 + 2OH^-$   
Na<sup>+</sup> + OH<sup>-</sup>  $\rightleftharpoons$  NaOH  
At anode:  $2Cl^- \longrightarrow Cl_2 + 2e$ 

The solution containing NaOH and NaCl as impurity is taken out and evaporated to dryness.

(ii) Castner-Kellner cell: This is the common cell in which mercury is used as cathode. The advantage of using Hg as a cathode is that the discharge potential of Na<sup>+</sup> ions is less than that of H<sup>+</sup> ions. Na<sup>+</sup> ions get discharged on mercury and sodium so deposited combines with mercury to form sodium amalgam. The cell consists of a large rectangular trough divided into three compartments by slate partitions which do not touch the bottom of the cell but dipping in mercury as shown in the (Fig. 6.7).

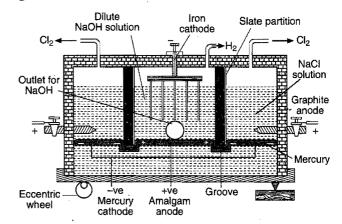


Fig. 6.7 Castner-Kellner cell

The mercury can flow from one compartment into other but the solution kept in one compartment cannot flow into other. Sodium chloride solution is placed in the two outer compartments and a dilute solution of sodium hydroxide in the inner compartment. Two graphite electrodes which act as anodes are fixed in the outer compartments and a series of iron rods fitted in the inner compartment act as cathode. Mercury in the outer compartments acts as cathode while in the inner compartment it acts as anode by induction. The cell is kept rocking with the help of an eccentric wheel.

When electricity is circulated, sodium chloride in the outer compartments is electrolysed. Chlorine is evolved at the graphite anode while Na<sup>+</sup> ions are discharged at the Hg cathode. The liberated sodium forms amalgam with mercury.

NaCl  $\rightleftharpoons$  Na<sup>+</sup> + Cl<sup>-</sup> At anode:  $2Cl^- \longrightarrow 2Cl + 2e \longrightarrow Cl_2$ 

At cathode :  $Na^+ + e \longrightarrow Na$ 

 $Na + Hg \longrightarrow Amalgam$ 

The sodium amalgam thus formed comes in the inner compartment due to rocking. Here, the sodium amalgam acts as the anode and iron rods act as cathode.

At anode: Na-amalgam  $\longrightarrow$  Na<sup>+</sup> + Hg + e At cathode:  $2H_2O + 2e \longrightarrow 2OH^- + H_2\uparrow$ 

The concentrated solution of sodium hydroxide (about 20%) is taken out from inner compartment and evaporated to dryness to get solid NaOH.

(iii) Solvay-Kellner cell: This is the modified cell. This cell has no compartments. The flowing mercury as shown in Fig. 6.8 acts as cathode. A number of graphite rods dipping in sodium chloride solution act as anode. A constant level of sodium chloride solution (brine) is maintained in the cell. On electrolysis chlorine gas is liberated at anode and Na<sup>+</sup> ions are discharged at cathode (mercury). Sodium discharged dissolves in Hg and forms sodium amalgam.

$$2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{l}$$
 (anode reaction)  
 $2\text{Na} + 2\text{Hg} + 2e \longrightarrow 2\text{Na} \cdot \text{Hg}$  (cathode reaction)

This amalgam flows out in a vessel containing water. Sodium hydroxide is formed with evolution of hydrogen.

$$2\text{Na}\cdot\text{Hg} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + 2\text{Hg} + \text{H}_2\uparrow$$

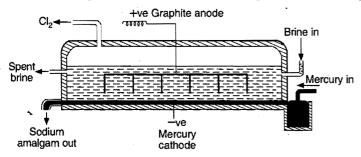


Fig. 6.8 Solvay-Kellner cell

(iv) Diaphragm cell: Most modern method for the production of sodium hydroxide from brine (aqueous sodium

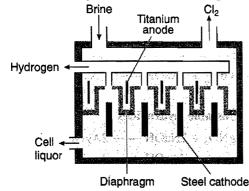


Fig. 6.9 A diaphragm cell for the electrolytic production of sodium hydroxide from brine (aqueous sodium chloride solution)

chloride solution) uses a diaphragm cell, containing steel and titanium electrodes which are separated by porous diaphragms to isolate the products. The process produces chlorine and hydrogen as well as sodium hydroxide.

$$2NaCl + 2H_2O \longrightarrow 2NaOH + Cl_2 + H_2$$

The porous diaphragm prevents the chlorine from mixing with the hydrogen and sodium hydroxide. The liquid is drawn off and the water is partially evaporated. The unconverted sodium chloride crystallizes, leaving the sodium hydroxide in solution.

#### Preparation of pure sodium hydroxide

Commercial sodium hydroxide is purified with the help of alcohol. Sodium hydroxide dissolves in alcohol while impurities like NaCl, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, etc., remain insoluble. The alcoholic filtrate is distilled. The alcohol distills off while pure solid sodium hydroxide is left behind.

#### Properties

**Physical Properties:** (a) It is a white crystalline solid. It has soapy touch.

- (b) It is highly deliquescent.
- (c) Its density is 2.13 g/mL and melting point 318.4°C.
- (d) It is highly soluble in water. It is bitter in taste.
- (e) It is corrosive in nature.
- (f) Its solubility is comparatively less in alcohol.

Chemical Properties: (a) Reactivity towards atmosphere: It cannot be kept in atmosphere. It absorbs moisture and carbon dioxide from atmosphere and converted into sodium carbonate.

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

**(b) Strong alkali:** Sodium hydroxide is a strong alkali as it dissociates completely in water furnishing Na<sup>+</sup> and OH<sup>-</sup> ions.

$$NaOH \implies Na^+ + OH^-$$

(i) It reacts with acids forming corresponding salts.

$$\begin{array}{c} \text{NaOH} + \text{HCl} & \longrightarrow \text{NaCl} + \text{H}_2\text{O} \\ 2\text{NaOH} + \text{H}_2\text{SO}_4 & \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \\ \text{NaOH} + \text{HNO}_3 & \longrightarrow \text{NaNO}_3 + \text{H}_2\text{O} \\ 3\text{NaOH} + \text{H}_3\text{PO}_4 & \longrightarrow \text{Na}_3\text{PO}_4 + 3\text{H}_2\text{O} \\ \text{NaOH} + \text{CH}_3\text{COOH} & \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} \end{array}$$

(ii) It combines with acidic oxides to form salts.

2NaOH + CO<sub>2</sub> 
$$\longrightarrow$$
 Na<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O
Sodium carbonate

2NaOH + SO<sub>2</sub>  $\longrightarrow$  Na<sub>2</sub>SO<sub>3</sub> + H<sub>2</sub>O
Sodium sulphite

2NaOH + 2NO<sub>2</sub>  $\longrightarrow$  NaNO<sub>3</sub> + NaNO<sub>2</sub> + H<sub>2</sub>O
Sodium sodium solitate

(iii) Amphoteric oxides of aluminium, zinc, tin and lead dissolve in sodium hydroxide forming corresponding salts.

$$\begin{array}{c} \text{Al}_2\text{O}_3 + 2\text{NaOH} \longrightarrow & 2\text{NaAlO}_2 + \text{H}_2\text{O} \\ \text{Sodium meta-aluminate} \\ \\ \text{ZnO} + 2\text{NaOH} \longrightarrow & \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O} \\ \text{Sodium zincate} \\ \\ \text{SnO} + 2\text{NaOH} \longrightarrow & \text{Na}_2\text{SnO}_2 + \text{H}_2\text{O} \\ \text{Sodium stannite} \\ \\ \text{SnO}_2 + 2\text{NaOH} \longrightarrow & \text{Na}_2\text{SnO}_3 + \text{H}_2\text{O} \\ \text{Sodium stannate} \\ \\ \text{PbO} + 2\text{NaOH} \longrightarrow & \text{Na}_2\text{PbO}_2 + \text{H}_2\text{O} \\ \text{Sodium plumbite} \\ \\ \text{PbO}_2 + 2\text{NaOH} \longrightarrow & \text{Na}_2\text{PbO}_3 + \text{H}_2\text{O} \\ \\ \text{Sodium plumbate} \\ \end{array}$$

- (c) Reactivity towards non-metals: Non-metals like halogens, P (yellow), S, Si, B, etc., are attacked by NaOH.
- (i) Halogens: Hypohalites and halides are formed by reaction of halogens with cold and dilute solution of NaOH.

$$\begin{array}{c} \text{Cl}_2 + 2\text{NaOH} & \longrightarrow \text{NaCl} + & \text{NaClO} & + \text{H}_2\text{O} \\ \text{(cold and dilute)} & & \text{Sodium hypo-chlorite} \\ \\ \text{Br}_2 + 2\text{NaOH} & \longrightarrow \text{NaBr} + & \text{NaBrO} & + \text{H}_2\text{O} \\ \text{(cold and dilute)} & & \text{Sodium hypo-bromite} \\ \\ \text{I}_2 + 2\text{NaOH} & \longrightarrow \text{NaI} + & \text{NaIO} & + \text{H}_2\text{O} \\ \text{(cold and dilute)} & & \text{Sodium hypo-iodite} \\ \end{array}$$

Halogens form halates and halides with hot and concentrated solution of NaOH.

$$3\text{Cl}_2 + 6\text{NaOH} \longrightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$$
(hot and conc.)

 $3\text{Br}_2 + 6\text{NaOH} \longrightarrow 5\text{NaBr} + \text{NaBrO}_3 + 3\text{H}_2\text{O}$ 
(hot and conc.)

 $3\text{I}_2 + 6\text{NaOH} \longrightarrow 5\text{NaI} + \text{NaIO}_3 + 3\text{H}_2\text{O}$ 
(hot and conc.)

 $3\text{Sodium bromate}$ 
 $3\text{Sodium iodate}$ 

(ii) Yellow phosphorus (white) when heated with NaOH solution evolves phosphine gas (PH<sub>3</sub>) along with the formation of sodium hypophosphite.

P<sub>4</sub> + 3NaOH + 3H<sub>2</sub>O 
$$\longrightarrow$$
 3NaH<sub>2</sub>PO<sub>2</sub> + PH<sub>3</sub> Sodium Phosphine hypophosphite

(iii) Sulphur on heating with sodium hydroxide solution forms sodium thiosulphate.

$$\begin{array}{c} \text{4S + 6NaOH} \longrightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{S} + 3\text{H}_2\text{O} \\ \text{Sodium thio-} \\ \text{sulphate} & \text{sulphide} \end{array}$$

(iv) Silicon evolves hydrogen when heated with NaOH solution.

$$2NaOH + Si + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$
  
Sodium silicate

(v) Boron also evolves hydrogen when fused with NaOH.

$$\begin{array}{ccc} 2B + 6NaOH & \longrightarrow & 2Na_3BO_3 & + & 3H_2 \\ & & \text{Sodium borate} \end{array}$$

(d) Reactivity towards metals: Metals like Zn, Al, Sn, Pb react with sodium hydroxide solution and evolve hydrogen.

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$
  
 $2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$   
 $Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2$   
 $Pb + 2NaOH + H_2O \longrightarrow Na_2PbO_3 + 2H_2$ 

[However, Sn and Pb when fused with NaOH form Na<sub>2</sub>SnO<sub>2</sub> and Na<sub>2</sub>PbO<sub>2</sub>, respectively.

$$Sn + 2NaOH \longrightarrow Na_2SnO_2 + H_2$$
  
 $Pb + 2NaOH \longrightarrow Na_2PbO_2 + H_2$ 

- (e) Action on salts: Sodium hydroxide reacts with metallic salts to form hydroxides which may be insoluble or dissolve in excess of NaOH to form salts of oxyacids. Some of the hydroxides decompose into insoluble oxides.
- (i) Insoluble hydroxides: Salts of nickel, iron, manganese, copper, etc., form insoluble hydroxides.

$$\begin{array}{c} \text{Ni}(\text{NO}_3)_2 \,+\, 2\text{NaOH} \longrightarrow \text{Ni}(\text{OH})_2 \,+\, 2\text{NaNO}_3 \\ \\ \text{FeSO}_4 \,+\, 2\text{NaOH} \longrightarrow \text{Fe}(\text{OH})_2 \,+\, \text{Na}_2\text{SO}_4 \\ \\ \text{FeCl}_3 \,+\, 3\text{NaOH} \longrightarrow \text{Fe}(\text{OH})_3 \,+\, 3\text{NaCl} \\ \\ \text{Red ppt}, \\ \\ \text{CrCl}_3 \,+\, 3\text{NaOH} \longrightarrow \text{Cr}(\text{OH})_3 \,+\, 3\text{NaCl} \\ \\ \text{Green ppt}, \\ \\ \text{MnSO}_4 \,+\, 2\text{NaOH} \longrightarrow & \text{Mn}(\text{OH})_2 \,+\, \text{Na}_2\text{SO}_4 \\ \\ \text{Buff coloured ppt}, \\ \\ \text{CuSO}_4 \,+\, 2\text{NaOH} \longrightarrow & \text{Cu}(\text{OH})_2 \,+\, \text{Na}_2\text{SO}_4 \\ \\ \text{Blue coloured ppt}, \\ \end{array}$$

(ii) Insoluble hydroxides which dissolve in excess of NaOH:

$$ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2 + Na_2SO_4$$
White (insoluble)
$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$$
Sodium zincate
(soluble)
$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$$
White ppt.
$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$
Sodium meta-
aluminate (soluble)
$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$$
White ppt.
$$Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$$
Sodium stannite
(soluble)

(iii) Unstable hydroxides:

$$2 Ag NO_3 + 2 NaOH \longrightarrow 2 Ag OH + 2 NaNO_3$$

$$2 Ag OH \longrightarrow Ag_2O + H_2O$$

$$(Brown)$$

$$Hg Cl_2 + 2 NaOH \longrightarrow Hg (OH)_2 + 2 NaCl$$

$$Hg (OH)_2 \longrightarrow HgO + H_2O$$

$$(Yellow)$$

**(f) Reactivity towards ammonium salts:** Ammonium salts are decomposed on heating with sodium hydroxide solution with the evolution of ammonia gas.

$$NH_4Cl + NaOH \longrightarrow NH_3 \uparrow + NaCl + H_2O$$
  
 $(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 \uparrow + 2H_2O$ 

**(g) Reactivity towards carbon monoxide:** NaOH reacts with carbon monoxide under pressure at 150–200°C to form sodium formate.

NaOH + CO 
$$\xrightarrow{5-10}$$
 atm. HCOONa Sodium formate

(h) Caustic property: Sodium hydroxide breaks down the proteins of skin to a pasty mass. On account of this property, it is commonly called as Caustic soda.

#### **■** Uses

Sodium hydroxide is among the top ten industrial chemicals. It is an important industrial chemical because it is an inexpensive base for the production of other sodium salts. It is a strong base, and this property is useful in many applications. It is used:

- (i) as a reagent in the laboratory.
- (ii) in refining of petroleum.
- (iii) in the manufacture of soap.
- (iv) in the manufacture of sodium metal.
- (v) in the manufacture of paper and rayon.
- (vi) in the manufacture of dyes and drugs.
- (vii) as an absorber of gases.
- (viii) in the manufacture of sodium hypochlorite, sodium chlorate and sodium nitrite.
  - (ix) for mercerizing cotton.
- (x) In large quantities in the production of aluminium which depends on its reaction with the amphoteric aluminium hydroxide.

#### 4. Sodium Carbonate or Washing Soda (Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O)

Sodium carbonate ( $Na_2CO_3$ ) is the most important of all alkali salts in commercial use. It is one of the world's most important industrial chemicals. It occurs in the ashes of marine plants which used to be its only source upto 1790. It is also found as natural deposits like sajji in India and trona ( $Na_2CO_3\cdot NaHCO_3\cdot 2H_2O$ ) in Egypt. The world production of sodium carbonate now exceeds 30 million tonnes per year.

#### **Manufacture**

The first process for the manufacture of  $Na_2CO_3$  was invented by Le-Blanc in 1790. However, this process has become obsolete and has been replaced by modern methods. The most important one is Solvay process. The following are the three main processes for the manufacture of sodium carbonate:

- (a) Le-Blanc process,
- (b) Solvay ammonia soda process and
- (c) Electrolytic process.

#### (a) Le-Blanc process

The raw materials of this process are common salt (NaCl), sulphuric acid, coke and limestone (CaCO<sub>3</sub>). It involves the following steps:

(i) Conversion of NaCl into Na<sub>2</sub>SO<sub>4</sub>: The common salt is heated with calculated quantity of sulphuric acid (concentrated) in the furnace shown in Fig. 6.10.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$
Sodium hydrogen
sulphate

The pasty mass of NaHSO<sub>4</sub> is then raked out on the hearth of the furnace with common salt. The paste is heated at higher

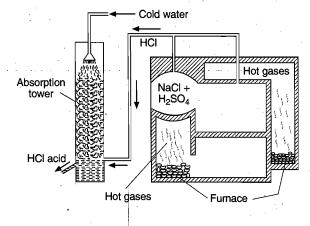


Fig. 6.10 Le-Blanc process

temperature when sodium hydrogen sulphate is converted into sodium sulphate.

$$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$$

Sodium sulphate, thus formed is technically called **salt cake**. The HCl evolved is dissolved in water to form hydrochloric acid.

(ii) Conversion of salt cake into black ash: The salt cake formed in the first step is broken into small pieces. These pieces are mixed with coke and limestone. The mixture is introduced into the cylindrical revolving furnace where it is strongly heated. Sodium sulphate is converted into sodium carbonate along with calcium sulphide with evolution of carbon monoxide according to the following reaction.

$$Na_2SO_4 + CaCO_3 + 4C \longrightarrow \underbrace{Na_2CO_3 + CaS}_{Black\ ash} + 4CO$$

The solid residue is called **black ash.** This contains about 45% sodium carbonate.

(iii) Recovery of Na<sub>2</sub>CO<sub>3</sub>: The black ash is crushed and extracted with water. The sodium carbonate dissolves and the insoluble impurities mainly consisting CaS are left behind. The insoluble material is called sludge or alkali waste. The solution consisting sodium carbonate is evaporated to get solid sodium carbonate.

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## (b) Solvay ammonia soda process

This is the modern process used for the manufacture of sodium carbonate worldwide, a large quantity of sodium carbonate is still produced by the **solvay process**. It is an industrial method for obtaining sodium carbonate from sodium chloride and limestone (CaCO<sub>3</sub>). The raw materials required in this process are the common salt, ammonia and limestone. In the main steps of this process, ammonia is 1st dissolved in a saturated solution of sodium chloride and then carbon dioxide is passed in it. The process involves the formation of a sparingly soluble sodium bicarbonate (baking soda) by the reaction of sodium chloride and ammonium bicarbonate in aqueous solution. The reactions taking place in the process are:

NH<sub>3</sub> + H<sub>2</sub>O + CO<sub>2</sub> 
$$\longrightarrow$$
 NH<sub>4</sub>HCO<sub>3</sub>
Ammonium
bicarbonate

NaCl + NH<sub>4</sub>HCO<sub>3</sub>  $\longrightarrow$  NaHCO<sub>3</sub> + NH<sub>4</sub>Cl
Sodium
bicarbonate

$$NH_3 + H_2O + CO_2 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$$

Sodium bicarbonate on heating decomposes into sodium carbonate.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

The various steps involved in the process are:

(i) Saturation of brine with ammonia: This step is done in ammonia absorber (Fig. 6.11). Ammonia from the ammonia generator is circulated through the solution. The ammonical brine solution is allowed to stand for some time as to allow any precipitate formed to settle down. Ammonia precipitates, the hydroxides of magnesium, iron, calcium, etc., if present as impurity in the common salt.

$$NH_3 + H_2O \longrightarrow NH_4OH$$
 $MgCl_2 + 2NH_4OH \longrightarrow Mg(OH)_2 + 2NH_4Cl_{ppt}$ 

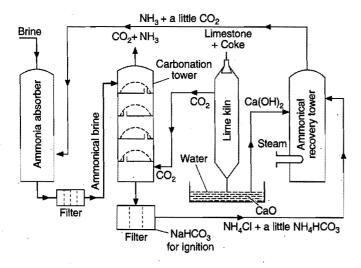


Fig. 6.11 Solvay ammonia soda process

Ammonia mixed with a little carbon dioxide if used, precipitates calcium and magnesium as carbonates.

$$CaCl_2 + 2NH_3 + H_2O + CO_2 \longrightarrow CaCO_3 + 2NH_4Cl_{ppt}$$

The clear liquid is now allowed to go into the carbonation tower.

(ii) Carbonation: Ammonical brine solution is cooled in the cooling pipe and then allowed to enter a little above the middle of the carbonation tower packed with perforated plates. It flows down slowly in the tower and meets with an upward stream of carbon dioxide. The sparingly soluble sodium bicarbonate (NaHCO<sub>3</sub>) gets precipitated. This is taken out from the tower.

$$NaCl + NH_3 + H_2O + CO_2 = NaHCO_3 + NH_4Cl$$

- (iii) Filtration: The solution obtained from carbonation tower is filtered with the help of rotatory vacuum filter. The filtrate is pumped to the top of recovery tower.
- (iv) Ammonia recovery: The filtrate from the vacuum filter contains ammonium chloride and a little ammonium bicarbonate. Ammonia is recovered from this filtrate by passing steam and adding Ca(OH)<sub>2</sub>. This ammonia is again used.

$$\begin{array}{c} \text{NH}_4\text{HCO}_3 \xrightarrow{\text{Heat}} \text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2 \\ 2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 &\longrightarrow 2\text{NH}_3 + \text{CaCl}_2 + 2\text{H}_2\text{O} \end{array}$$

(v) Calcination: Sodium bicarbonate obtained in step (ii) is strongly heated in especially designed cylindrical vessels when sodium carbonate is obtained.

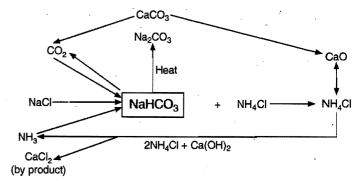
$$2\text{NaHCO}_3 \xrightarrow{250^{\circ}\text{C}} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

Carbon dioxide used in the carbonating tower is produced by heating limestone, CaCO<sub>3</sub>.

$$CaCO_3 \longrightarrow CaO + CO_2$$
Calcium oxide

The calcium oxide (CaO) produced from this process is known as quicklime or lime. It is dissolved in water to form calcium hydroxide which is used for the recovery of ammonia.

The byproduct of this process is calcium chloride. The process on the whole is cheap, self-contained and self-sufficient and the product formed, Na<sub>2</sub>CO<sub>3</sub>, is of high purity.



Flow Sheet of Solvay Process

## (c) Electrolytic process

In this process sodium chloride is first converted into sodium hydroxide by electrolysis. In the Nelson cell used for the manufacture of sodium hydroxide, carbon dioxide under pressure is blown along with steam. The sodium hydroxide produced will then react with carbon dioxide to form sodium carbonate. The solution is concentrated and crystallised.

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Sodium carbonate can also be made in the laboratory by neutralising sodium hydroxide solution with carbon dioxide. The solution on concentration and cooling deposits crystals of the decahydrate;  $Na_2CO_3 \cdot 10H_2O$ .

## Properties

**Physical Properties:** (a) Sodium carbonate is a white crystalline solid. It is known in several hydrated forms. The common form is decahydrate, Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O. This form is called **washing soda.** The decahydrate form on standing in air effloresces and crumbles to powder. It is the monohydrate form, Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O. It also forms a heptahydrate, Na<sub>2</sub>CO<sub>3</sub>·7H<sub>2</sub>O.

(b) On heating, the monohydrate changes into the anhydrous form which does not decompose on further heating even to redness. It is the amorphous powder and called **soda ash.** It melts at 852°C.

$$\begin{aligned} \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} & \xrightarrow{\text{below } 373\,\text{K}} \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} + 9\text{H}_2\text{O} \\ \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} & \xrightarrow{\text{above } 373\,\text{K}} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \\ & \text{Soda ash} \end{aligned}$$

(c) It is soluble in water with evolution of considerable amount of heat. The solution is alkaline in nature due to hydrolysis.

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$$

When the hot solution of sodium carbonate is concentrated and cooled, crystals of decahydrate form are obtained.

Chemical Properties: (a) Reaction with acids: It is readily decomposed by acids with evolution of carbon dioxide. The reaction occurs in two steps.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$
  
 $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$ 

(b) Reaction with CO<sub>2</sub>: On passing CO<sub>2</sub> through the concentrated solution of sodium carbonate, sodium bicarbonate gets precipitated.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

(c) Reaction with silica: When the mixture of sodium carbonate and silica is fused, sodium silicate is formed.

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$

Sodium silicate is called **soluble glass** or **water glass** as it is soluble in water.

(d) Reaction with slaked lime: Sodium hydroxide is formed when the solution of sodium carbonate and slaked lime, Ca(OH)<sub>2</sub>, is heated.

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$

(e) Reaction with sulphur and sulphur dioxide: When aqueous solution of sodium carbonate containing sulphur is treated with sulphur dioxide, sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) is formed.

$$Na_2CO_3 + SO_2 \xrightarrow{H_2O} Na_2SO_3 + CO_2 \uparrow$$
  
 $Na_2SO_3 + S \longrightarrow Na_2SO_3$ 

(f) Action on salts of non-alkali metals: Sodium carbonate reacts with metal salts (except alkali metal salts) to form insoluble normal or basic carbonates.

$$\begin{aligned} \text{CaCl}_2 + \text{Na}_2\text{CO}_3 &\longrightarrow \text{CaCO}_3 + 2\text{NaCl} \\ \text{BaCl}_2 + \text{Na}_2\text{CO}_3 &\longrightarrow \text{BaCO}_3 + 2\text{NaCl} \\ 2\text{MgCl}_2 + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} &\longrightarrow \text{MgCO}_3 \cdot \text{Mg(OH)}_2 + 4\text{NaCl} \\ & \text{Basic magnesium} &+ \text{CO}_2 \end{aligned}$$

$$5ZnSO_4 + 5Na_2CO_3 + 4H_2O \longrightarrow$$

$$[2ZnCO_3 \cdot 3Zn(OH)_2] \cdot H_2O + 5Na_2SO_4 + 3CO_2$$
Basic zinc carbonate

$$CuSO_4 + Na_2CO_3 \longrightarrow CuCO_3 + Na_2SO_4$$

$$2CuSO_4 + 2Na_2CO_3 + H_2O \longrightarrow Cu(OH)_2 \cdot CuCO_3 + CO_2 + Na_2SO_4$$
Basic copper carbonate

$$3(CH_3COO)_2Pb + 3Na_2CO_3 + H_2O \longrightarrow \\ 2PbCO_3Pb(OH)_2 + CO_2 + 6CH_3COONa \\ Basic lead carbonate \\ .$$

$$2AgNO_3 + Na_2CO_3 \longrightarrow Ag_2CO_3 + 2NaNO_3$$

Carbonates of metals like Fe, Al, Sn, etc., when formed are immediately hydrolysed to hydroxides.

$$Fe_2(SO_4)_3 + 3Na_2CO_3 \longrightarrow Fe_2(CO_3)_3 + 3Na_2SO_4$$
$$Fe_2(CO_3)_3 + 3H_2O \longrightarrow 2Fe(OH)_3 + 3CO_2$$

## ■ Uses

Sodium carbonate is used:

- (i) in the manufacture of soaps, detergents, dyes, drugs and other chemicals.
  - (ii) in laundries and in softening of water as washing soda.
- (iii) in the manufacture of glass, sodium silicate, paper, borax, soap powders, caustic soda, etc.
- (iv) as a laboratory reagent. The mixture of  $Na_2CO_3$  and  $K_2CO_3$  is used as a fusion mixture. It is used in quantitative analysis to standardise acid solutions. In qualitative analysis, it is used in the detection of acidic radicals especially of insoluble salts.
  - (v) in textile, petroleum refining, paints and dyes.
  - (vi) for the preparation of various carbonates of metals.

## 5. Sodium bicarbonate (Baking soda), NaHCO<sub>3</sub>

**Preparation:** Sodium hydrogen carbonate, NaHCO<sub>3</sub> (Sodium bicarbonate), is commonly called **bicarbonate of soda** or **baking soda**. It is obtained as the intermediate product in the solvay ammonia soda process. Normal carbonate can be changed to bicarbonate by passing carbon dioxide through its saturated solution.

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$
Sparingly soluble

**Properties:** It is a white crystalline solid, sparingly soluble in water. The solution is alkaline in nature due to hydrolysis. The solution is weakly basic.

$$NaHCO_3 + H_2O \implies NaOH + H_2CO_3$$

The solution gives yellow colour with methyl orange but no colour with phenolphthalein.

On heating, it loses carbon dioxide and water forming sodium carbonate.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

The metal salt which forms basic carbonate with sodium carbonate, gives normal carbonate with sodium bicarbonate.

$$ZnSO_4 + 2NaHCO_3 \longrightarrow ZnCO_3 + Na_2SO_4 + H_2O + CO_2$$

## Uses

- (i) It is used as a medicine (sodabicarb) to neutralise the acidity in the stomach.
- (ii) It is largely used for making baking powder. Baking powder is a mixture of potassium hydrogen tartrate and sodium bicarbonate. Baking powder is also prepared by using NaHCO<sub>3</sub> (30%), starch (40%), calcium hydrogen phosphate (10%) and NaAl(SO<sub>4</sub>)<sub>2</sub>.
  - (iii) It is used in making effervescent drinks.
  - (iv) It is used in fire extinguishers.
  - (v) It is used for production of carbon dioxide.

## 6. Sodium Thiosulphate, (Hypo), Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O

It is the sodium salt of an unstable acid, thiosulphuric acid  $(H_2S_2O_3)$ . It is also known as **hypo.** The following methods can be used for its preparation.

(i) It is obtained by boiling sodium sulphite solution with flowers of sulphur.

$$\begin{array}{cccc} Na_2SO_3 & + & S & \longrightarrow & Na_2S_2O_3 \\ Sodium & Sulphur & Sodium \\ sulphite & & thiosulphate \end{array}$$

The unreacted sulphur is filtered off and the filtrate is evaporated to crystallisation.

(ii) Spring's reaction: The mixture of sodium sulphite and sodium sulphide is treated with calculated quantity of iodine.

$$Na_2S + I_2 + Na_2SO_3 \longrightarrow Na_2S_2O_3 + 2NaI$$

The resulting solution is concentrated and allowed to crystallise when crystals of sodium thiosulphate being less soluble separate out first.

(iii) When the solution containing sodium carbonate and sodium sulphide is treated with sulphur dioxide, sodium thiosulphate is formed with evolution of carbon dioxide.

$$2Na_2S + Na_2CO_3 + 4SO_2 \longrightarrow 3Na_2S_2O_3 + CO_2 \uparrow$$

(iv) Sodium thiosulphate is formed when sulphur is heated with caustic soda solution.

$$4S + 6NaOH \longrightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$$

With excess of sulphur, sodium pentasulphide is formed,

$$Na_2S + 4S \longrightarrow Na_2S_5$$

(v) On passing SO<sub>2</sub> gas through the solution of Na<sub>2</sub>CO<sub>3</sub> in presence of sulphur we get sodium thiosulphate.

$$Na_2CO_3 + SO_2 \longrightarrow Na_2SO_3 + CO_2$$
  
 $Na_2SO_3 + S \longrightarrow Na_2S_2O_3$ 

## **Properties**

- (i) It is a colourless crystalline solid consisting of 5 molecules of water as water of crystallisation. It has the formula, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O. It is soluble in water. It melts at 48°C.
- (ii) Action of heat: It is efflorescent substance. The water molecules are completely lost when heated at 215°C.

$$Na_2S_2O_3 \cdot 5H_2O \xrightarrow{215^{\circ}C} Na_2S_2O_3 + 5H_2O$$

When strongly heated above 223°C, it decomposes forming sodium sulphate (salt cake) and sodium pentasulphide.

$$4Na_2S_2O_3 \longrightarrow 3Na_2SO_4 + Na_2S_5$$

(iii) Reaction with acids: Dilute acids decompose it with evolution of SO<sub>2</sub> and precipitation of sulphur.

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + S + H_2O$$
  
 $Na_2S_2O_3 + H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + S + H_2O$ 

(iv) Oxidation: It is oxidised by iodine quantitatively.

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$
Sodium
tetrathionate

In this reaction, colour of iodine disappears.

(v) Reducing action: It is oxidised by chlorine and bromine water. Sulphur is precipitated.

$$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl + S$$
  
It reduces FeCl<sub>3</sub> to FeCl<sub>2</sub>

$$2Na_2S_2O_3 + 2FeCl_3 \longrightarrow Na_2S_4O_6 + 2FeCl_2 + 2NaCl$$

(vi) Reaction with AgNO<sub>3</sub>: A white precipitate of silver thiosulphate is obtained which changes to yellow, brown and finally black due to the formation of silver sulphide.

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$$
  
 $Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$ 

(vii) Reaction with silver halides: Halides form complexes with sodium thiosulphate. Silver bromide forms argentothiosulphate complex.

Similar reactions are observed with AgCl and AgI.

This property is utilised in photography for fixing the negative and positive of black and white photography. It removes undecomposed AgBr present on the film.

(viii) Reaction with copper sulphate: Cuprous thiosulphate is formed which dissolves in excess of sodium thiosulphate to form a complex.

$$\begin{array}{c} \text{CuSO}_4 \,+\, \text{Na}_2\text{S}_2\text{O}_3 &\longrightarrow \text{CuS}_2\text{O}_3 \,+\, \text{Na}_2\text{SO}_4 \\ & \text{Cupric} \\ \text{thiosulphate} \\ \\ 2\text{CuS}_2\text{O}_3 \,+\, \text{Na}_2\text{S}_2\text{O}_3 &\longrightarrow \text{Cu}_2\text{S}_2\text{O}_3 \,+\, \text{Na}_2\text{S}_4\text{O}_6 \\ & \text{Cuprous} \\ \text{thiosulphate} \\ \\ 3\text{Cu}_2\text{S}_2\text{O}_3 \,+\, 2\text{Na}_2\text{S}_2\text{O}_3 &\longrightarrow \begin{array}{c} \text{Na}_4[\text{Cu}_6(\text{S}_2\text{O}_3)_5] \\ \text{Sodium} & \text{cuprothiosulphate} \end{array}$$

## Uses

Sodium thiosulphate is used:

- (i) as an antichlor to remove excess of chlorine from bleached fabrics.
  - (ii) in the extraction of silver and gold.
  - (iii) in photography as a fixing agent in the name of hypo.
- (iv) as a reagent in iodometric and iodimetric titrations for the estimation of iodine, CuSO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KMnO<sub>4</sub>, Na<sub>3</sub>AsO<sub>3</sub>, etc.

## **■ 7. Microcosmic Salt, Na(NH<sub>4</sub>)HPO<sub>4</sub>·4H<sub>2</sub>O**

**Preparation:** It is prepared by dissolving ammonium chloride and disodium hydrogen phosphate in molecular proportion in hot water.

$$NH_4Cl + Na_2HPO_4 + 4H_2O \longrightarrow NaNH_4HPO_4 \cdot 4H_2O + NaCl$$

The sparingly soluble microcosmic salt separates out. It is filtered and purified by recrystallisation.

## **Properties**

- (i) It is colourless crystalline solid, sparingly soluble in water.
- (ii) When heated, it melts to form a clear transparent mass which has the property of combining with metallic oxides to form coloured orthophosphates.

$$Na(NH_4)HPO_4 \longrightarrow NaPO_3 + NH_3 + H_2O$$
Sodium
metaphosphate

 $NaPO_3 + CuO \longrightarrow NaCuPO_4$ 
Blue mass

On account of this property, microcosmic salt is used for the detection of coloured ions. The test is similar to borax bead test. The salt is heated on a loop of a platinum wire, a transparent bead is formed. When hot bead is brought in contact with coloured substance and strongly heated, a coloured bead is formed if the substance contains Cu<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, etc.

Uses: It is especially used for testing silica with which a cloudy bead containing floating properties of silica is obtained.

## **8.** Sodium Chloride (Common Salt), NaCl

Sodium chloride is the most common of the salts of sodium. It is also called common salt, table salt, rock salt or sea salt. An aqueous solution of sodium chloride is known as **brine**. Sea water contains about 2.95 per cent sodium chloride. As a rock salt it is found at several places in England, Australia, Germany, Canada, Pakistan (Khewra—Punjab) and India (Mandi—Himachal Pradesh). It is found in land lakes (e.g., Sambhar lake in India, lake Elton in Russia).

## Manufacture from sea water

In tropical countries like India, on the sea coasts, the sea water is allowed to dry up under summer heat in small tanks or pits. The solid crust so formed is collected.

In very cold countries, the sea water is concentrated by freezing. The concentrated solution is then evaporated in big iron pans. Sodium chloride thus obtained contains impurities like magnesium chloride, calcium chloride, etc. It is purified by passing hydrogen chloride through a saturated solution of the commercial salt. The precipitation of sodium chloride occurs due to common ion effect.

## **Properties**

- (a) It is a white crystalline solid. It is slightly hygroscopic.
- (b) Its density is 2.17 g/mL when pure. It melts at 800°C. It is soluble in water. It dissolves in water with absorption of heat.
  - (c) It is insoluble in alcohol.
- (d) The common salt is the starting material for the preparation of all the other sodium compounds and extraction of sodium. Sodium, sodium hydroxide and sodium carbonate are the three main materials obtained from common salt which are then used to prepare other important compounds of sodium.

## **Uses**

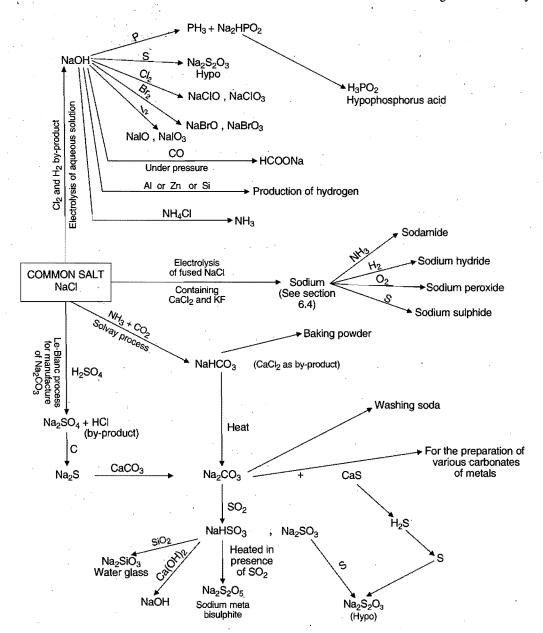
- (i) It is an essential constituent of food.
- (ii) It is used as a preservative of food articles like fish, meat, etc.
  - (iii) It is used for making useful sodium compounds.
- (iv) It finds application in salting out of soap, and in making freezing mixtures.
  - (v) Impure salt (rock salt) is used to de-ice roads.

## 9. Sodium Cyanide, NaCN

It is manufactured by the following methods:

(i) **From sodium:** Sodamide is first formed by passing dry ammonia gas over heated sodium in iron retorts at 300-400°C.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2 \uparrow$$



Flowsheet chart for the properties of sodium chloride and preparation of various compounds of sodium

The molten sodamide thus obtained is dropped on red hot charcoal when first sodium cyanamide and then sodium cyanide is formed.

$$2NaNH_2 + C \longrightarrow Na_2CN_2 + 2H_2$$

$$Na_2CN_2 + C \longrightarrow 2NaCN$$

$$2NaNH_2 + 2C \longrightarrow 2NaCN + 2H_2$$
or
$$NaNH_2 + C \longrightarrow NaCN + H_2$$

(ii) From calcium cyanamide: NaCN is prepared by fusing a mixture of crude calcium cyanamide (nitrolim) and sodium carbonate in the presence of carbon.

$$CaCN_2 + C + Na_2CO_3 \longrightarrow 2NaCN + CaCO_3$$

The fused product is extracted with water and the solution on evaporation gives NaCN.

(iii) From gas works: Coal gas is always contaminated with some hydrocyanic acid and ammonia. Before it is put into use, it is passed through copper sulphate solution when ammonium tricyanocuprate (I) is formed.

$$2\text{CuSO}_4 + 4\text{HCN} \longrightarrow 2\text{CuCN} + (\text{CN})_2 + 2\text{H}_2\text{SO}_4$$
  
 $N\text{H}_3 + \text{HCN} \longrightarrow N\text{H}_4\text{CN}$   
 $2N\text{H}_4\text{CN} + \text{CuCN} \longrightarrow (N\text{H}_4)_2[\text{Cu(CN})_3]$ 

The complex is decomposed by the addition of dilute H<sub>2</sub>SO<sub>4</sub> and the evolved HCN is absorbed in caustic soda.

$$\begin{aligned} (NH_4)_2[Cu(CN)_3] + H_2SO_4 & \longrightarrow (NH_4)_2SO_4 + CuCN + 2HCN \\ NaOH + HCN & \longrightarrow NaCN + H_2O \end{aligned}$$

## **Properties**

It is a white crystalline solid. It has a characteristic smell and highly poisonous in nature. It is soluble in water and its solution is alkaline due to hydrolysis.

It forms complex cyanides with the salts of copper, silver, gold, cadmium, zinc, iron, cobalt, nickel, etc. Some examples are given below:

(i) 
$$AgNO_3 + NaCN \longrightarrow AgCN + NaNO_3$$
  
 $AgCN + NaCN \longrightarrow Na[Ag(CN)_2]$ 

(ii) 
$$CdSO_4 + 2NaCN \longrightarrow Cd(CN)_2 + Na_2SO_4$$
  
 $Cd(CN)_2 + 2NaCN \longrightarrow Na_2[Cd(CN)_4]$ 

(iii) FeSO<sub>4</sub> + 2NaCN 
$$\longrightarrow$$
 Na<sub>2</sub>SO<sub>4</sub> + Fe(CN)<sub>2</sub>  
Fe(CN)<sub>2</sub> + 4NaCN  $\longrightarrow$  Na<sub>4</sub>[Fe(CN)<sub>6</sub>]

(iv) 
$$CuSO_4 + 2NaCN \longrightarrow Na_2SO_4 + Cu(CN)_2$$
  
 $2Cu(CN)_2 \longrightarrow 2CuCN + (CN)_2$   
 $CuCN + 3NaCN \longrightarrow Na_3[Cu(CN)_4]$ 

A dilute solution of sodium cyanide dissolves gold and silver in presence of oxygen.

$$4Au + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Au(CN)_2] + 4NaOH$$

## Uses

Sodium cyanide is used:

- (i) in the extraction of Ag and Au.
- (ii) as germicide in agriculture.
- (iii) in electroplating of silver, gold, etc.
- (iv) in the preparation of complex cyanides of transition metals and organic cyanides.
  - (v) as a laboratory reagent.

## 6.6 POTASSIUM

Potassium is not found in the native state. In combined state, potassium compounds are widely distributed in nature almost to the same extent as the sodium compounds. All plants contain considerable amounts of potassium compounds which they receive from soil. Its compounds occur as salt beds, in rocks and in sea water. The important minerals of potassium are:

Sylvite KCl

Carnallite  $KCl \cdot MgCl_2 \cdot 6H_2O$ 

Kainite KCl·MgSO<sub>4</sub>·MgCl<sub>2</sub>·3H<sub>2</sub>O

Indian saltpetre KNO<sub>3</sub>

Feldspar  $K_2O \cdot Al_2O_3 \cdot 6SiO_2$  (clay) Polyhalite  $K_2SO_4 \cdot MgSO_4 \cdot CaSO_4 \cdot 6H_2O$ 

Metallic potassium is not of much in demand as cheaper sodium can be used for the same purpose. Potassium is prepared by the chemical reduction of potassium chloride, KCl rather than by electrolysis of the molten chloride, as in the preparation of sodium. However, it can also be prepared by carrying electrolysis of fused potassium hydroxide or by electrolysis of fused mixture of KCl and CaCl<sub>2</sub>. Potassium is manufactured by reducing the fluoride with calcium carbide at 1000°C in steel cylinders.

$$2KF + CaC_2 \xrightarrow{1000^{\circ}C} 2K + CaF_2 + 2C$$

The metal obtained is 99.7 per cent pure.

**Uses:** (i) Potassium is used in photoelectric cells. In the commercial process, potassium chloride is melted with sodium metal by heating to 870°C.

$$KCl + Na \xrightarrow{870^{\circ} C} K + NaCl$$

At this temperature, potassium forms a vapour, which leaves the reaction chamber and then condensed in photoelectric cells.

(ii) An alloy of potassium and sodium is used in special thermometers employed for measuring high temperatures.

## Compounds of Potassium

## ■ 1. Potassium Chloride, KCl

Potassium chloride is the starting material for the preparation of various potassium compounds. It is obtained from carnallite, KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O, by fractional crystallisation. The carnallite is ground and extracted with a 20 per cent solution of MgCl<sub>2</sub>. The carnallite dissolves while NaCl and MgSO<sub>4</sub> remain undissolved. The clear solution is put to crystallisation when crystals of KCl separate out.

More than 90% of the potassium chloride that is mined is used directly as a plant fertilizer. The rest is used in the preparation of various potassium compounds.

## ■ 2. Potassium Iodide, KI

## Preparation

(i) It is prepared by the action of hydroiodic acid on potassium hydroxide or potassium carbonate.

$$\begin{aligned} &KOH + HI \longrightarrow KI + H_2O \\ &K_2CO_3 + 2HI \longrightarrow 2KI + CO_2 + H_2O \end{aligned}$$

(ii) It may be prepared by heating iodine with hot and concentrated solution of potassium hydroxide. The resulting liquid consisting of KI and KIO<sub>3</sub> is evaporated to dryness and the solid residue is then ignited with powdered charcoal to convert iodate also into iodide.

$$3I_2 + 6KOH \longrightarrow 5KI + KIO_3 + 3H_2O$$
  
 $KIO_3 + 3C \longrightarrow KI + 3CO$ 

The mass is extracted with water, filtered and the clear solution is evaporated to dryness.

(iii) Potassium iodide is obtained on large scale by the action of ferroso ferric iodide on potassium carbonate. The solution is boiled.

$$4K_2CO_3 + Fe_3I_8 + 4H_2O \longrightarrow 8KI + 4CO_2 + Fe(OH)_2 \cdot 2Fe(OH)_3$$

 $[\text{Fe}_3 I_8 \text{ is formed separately by adding iodine to iron fillings in water.}$ 

Fe + 
$$I_2 \longrightarrow FeI_2$$
  
 $3FeI_2 + I_2 \longrightarrow Fe_3I_8$  (ferroso ferric iodide)]

The precipitate is filtered off and the clear solution is put to crystallisation when crystals of potassium iodide are obtained.

[Note: KBr, potassium bromide is obtained similarly by the application of above methods.]

## **Properties**

- (a) It is white crystalline solid, highly soluble in water and alcohol.
- (b) It dissolves in free iodine and forms potassium tri-iodide.

[The solubility of iodine increases in presence of potassium iodide.]

$$KI + I_2 \longrightarrow KI_3 \rightleftharpoons KI + I_2$$

Kì<sub>3</sub> is unstable and gives up extra iodine readily.

(c) Sulphuric acid decomposes potassium iodide.

$$2KI + H2SO4 \longrightarrow K2SO4 + 2HI$$

$$2HI + H2SO4 \longrightarrow 2H2O + I2 + SO2$$

$$2KI + 2H2SO4 \longrightarrow K2SO4 + I2 + SO2 + 2H2O$$

$$2KI + 3H2SO4 \longrightarrow 2KHSO4 + I2 + SO2 + 2H2O$$

(d) Chlorine liberates iodine from potassium iodide.

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

(e) It acts as a reducing agent. Oxidising agents like acidified KMnO<sub>4</sub>, acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, CuSO<sub>4</sub>, etc., liberate iodine from KI.

(i) 
$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
  
 $[2KI + H_2SO_4 + O \rightarrow K_2SO_4 + H_2O + I_2] \times 5$ 

$$2KMnO_4 + 10KI + 8H_2SO_4 \rightarrow 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O_4$$

(ii) 
$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$
  
 $[2KI + H_2SO_4 + O \rightarrow K_2SO_4 + H_2O + I_2] \times 3$ 

$$6KI + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$

(iii) 
$$[CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4] \times 2$$
  
Unstable

The above three reactions are used in iodometric titrations.

(iv) 
$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$
  
 $2KI + 2HNO_3 + O \longrightarrow 2KNO_3 + I_2 + H_2O$   
 $2KI + 4HNO_3 \longrightarrow 2KNO_3 + 2NO_2 + I_2 + 2H_2O$ 

(f) Potassium iodide forms insoluble iodides with AgNO<sub>3</sub> and lead salts.

$$\begin{array}{c} \text{AgNO}_3 + \text{KI} \longrightarrow \text{AgI} + \text{KNO}_3 \\ \text{Yellow} \\ \text{Pb}(\text{CH}_3\text{COO})_2 + 2\text{KI} \longrightarrow \begin{array}{c} \text{PbI}_2 + 2\text{CH}_3\text{COOK} \\ \text{Yellow} \end{array}$$

If forms a red precipitate with HgCl<sub>2</sub> which dissolves in excess of potassium iodide forming potassium mercuric iodide.

$$HgCl_2 + 2KI \longrightarrow HgI_2 + 2KCI$$
  
 $HgI_2 + 2KI \longrightarrow K_2HgI_4$ 

The alkaline solution of  $K_2HgI_4$  is called Nessler's reagent and is used for the detection and estimation of  $NH_4^+$  ion.

Uses: It is used:

- (a) as a solvent of iodine.
- (b) as a reagent in laboratory.
- (c) in medicine and photography.
- (d) for making Nessler's reagent in the laboratory.

## 3. Potassium Nitrate, KNO<sub>3</sub>

Potassium nitrate is prepared by the reaction of potassium hydroxide and nitric acid.

$$\begin{array}{c} KOH + HNO_3 \longrightarrow KNO_3 + H_2O \\ \text{Potassium} \\ \text{hydroxide} \end{array} \\ \begin{array}{c} \text{Nitric acid} \\ \text{nitrate} \end{array}$$

**Uses:** (i) KNO<sub>3</sub> is used in the production of fertilizers and for explosives and fireworks.

(ii) Potassium nitrate, KNO3, releases oxygen when heated,

$$2KNO_3(s) \xrightarrow{\Delta} 2KNO_2(s) + O_2(g)$$

and is used to facilitate the ignition of matches.

(iii) It is less hygroscopic (water absorbing) than the corresponding sodium compounds, because the K<sup>+</sup> cation is larger and is less strongly hydrated by H<sub>2</sub>O molecule.

## 4. Oxides

Three oxides of potassium are known:

- (a) potassium monoxide, K<sub>2</sub>O.
- (b) potassium dioxide (tetraoxide or superoxide),  $KO_2$  or  $K_2O_4$ .
  - (c) potassium sesquioxide, K<sub>2</sub>O<sub>3</sub>.
- (b) Potassium dioxide; (tetraoxide or superoxide) KO<sub>2</sub>: Almost all of the potassium metal produced is used in the preparation of potassium superoxide, KO<sub>2</sub>. It is prepared by burning potassium in excess of oxygen free from moisture.

$$K + O_2 \longrightarrow KO_2$$

It is also obtained by reacting dry potassium hydroxide with ozone.

$$2KOH + O_3 \longrightarrow 2KO_2 + H_2O$$

**Properties:** Potassium superoxide,  $KO_2$ , is a chrome yellow powder. It dissolves in water giving  $H_2O_2$  and  $O_2$ .

$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

It reacts directly with CO and CO<sub>2</sub>.

$$2KO_2 + CO \longrightarrow K_2CO_3 + O_2$$
  
 $4KO_2 + 2CO_2 \longrightarrow 2K_2CO_3 + 3O_2$ 

On heating with sulphur, it forms potassium sulphate.

$$2KO_2 + S \longrightarrow K_2SO_4$$

**Uses:** KO<sub>2</sub> is used as an oxidising agent. It is used as air purifier in space capsules, submarines and breathing masks as in all these it produces oxygen and removes carbon dioxide.

(c) Potassium sesquioxide;  $K_2O_3$ : It is obtained when oxygen is passed through liquid ammonia containing potassium.

4K (dissolved in liquid NH<sub>3</sub>) 
$$\xrightarrow{3O_2}$$
 2K<sub>2</sub>O<sub>3</sub>

Uses: It is used for the production of self contained breathing apparatus which is used in the situations such as fire fighting, where toxic fumes may be present.

## ■ 5. Potassium Hydroxide (Caustic Potash), KOH

It was first prepared from potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), obtained by leaching plant ashes with water and evaporating the solution in large pots (whence the name).

It is manufactured like sodium hydroxide, *i.e.*, by electrolysis of aqueous KCl solution.

Uses: It is an important base and is used for the absorption of gases like CO<sub>2</sub>, SO<sub>2</sub>, etc. It is often called as **caustic potash** and its aqueous solution is known as **potash lye.** It is used for making soft and liquid soaps.

Alcoholic caustic potash is a useful reagent in organic chemistry as it eliminates hydrogen halides from alkyl halides.

$$C_2H_5Br + KOH(alc.) \longrightarrow C_2H_4 + KBr + H_2O$$

Like caustic soda, NaOH caustic potash, KOH also is quite corrosive and destructive to the organic tissue; they convert animal fats to soaps.

## ■ 6. Potassium Carbonate, K<sub>2</sub>CO<sub>3</sub>

It is also called **Potash** or **Pearl ash.** It cannot be made by the use of Solvay process as potassium bicarbonate is more soluble than sodium bicarbonate. However, it can be prepared by **Le-Blanc process.** KCl is first converted into  $K_2SO_4$ . Potassium sulphate  $(K_2SO_4)$  is then heated with  $CaCO_3$  and carbon.

$$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$$
  
 $KHSO_4 + KCl \longrightarrow K_2SO_4 + HCl$ 

$$K_2SO_4 + CaCO_3 + 2C \longrightarrow K_2CO_3 + CaS + 2CO_2$$

It is a white powder, deliquescent in nature. It is highly soluble in water.

Uses: It is used in the manufacture of hard glass. The mixture of  $K_2CO_3$  and  $Na_2CO_3$  is used as a fusion mixture in laboratory.

## **Example 3.** Explain the following:

- (a) Sodium carbonate is made by Solvay process but the same process is not extended to the manufacture of potassium carbonate.
- (b) On exposure to air, sodium hydroxide becomes liquid and after sometimes it changes to white powder.
- (c) Alkali metals are obtained by the electrolysis of the molten salts and not by the electrolysis of their aqueous solutions.

- (d) Calcium chloride is added to NaCl in the electrolytic manufacture of sodium.
- (e) An aqueous solution of iodine becomes colourless on adding excess of sodium hydroxide solution.

## **Solution:**

- (a) KHCO<sub>3</sub>, the intermediate, is very soluble in water and cannot be obtained in solid state as NaHCO<sub>3</sub> is formed in Na<sub>2</sub>CO<sub>3</sub> manufacture.
- (b) Sodium hydroxide continuously absorbs carbon dioxide and moisture of atmosphere and is converted into sodium carbonate solution.

A stage reaches when the solution becomes saturated and the crystals are formed. These crystals, with the passage of time, lose water of crystallisation (efflorescence) and crumble to white powder.

(c) The solutions of alkali metal salts contain metal cations, H<sup>+</sup>, OH<sup>-</sup> and the anions. The discharge potential of H<sup>+</sup> ions is lower than the metal cations and thus, on electrolysis of solutions of alkali metal salts, hydrogen is discharged at cathode rather than the metal.

However, on electrolysis of molten salt, the metal cation only present gets discharged at cathode.

- (d) Pure sodium chloride melts at about 800°C. At this temperature both sodium and chlorine (products of electrolysis) are corrosive in nature. Sodium also forms a metallic fog at this temperature. To remove these difficulties, the fusion temperature is reduced to 600°C by adding CaCl<sub>2</sub>.
- (e) Iodine reacts with NaOH forming colourless compounds. Thus, the colour of iodine disappears on addition of NaOH.

$$2NaOH \, + \, I_2 \longrightarrow \underbrace{NaI + NaIO}_{Colourless \; products} \, + \, H_2O$$

Example 4. How would you prepare the following?

- (a) Sodium thiosulphate from sodium carbonate.
- (b) Microcosmic salt from disodium hydrogen phosphate.
- (c) Sodium carbonate from sodium chloride.
- (d) Sodium thiosulphate from sodium sulphite.
- (e) Sodium cyanide from metallic sodium.

## **Solution:**

(a) Sodium carbonate is first converted into sodium sulphite by passing sulphur dioxide.

$$Na_2CO_3 + SO_2 \longrightarrow Na_2SO_3 + CO_2$$

The solution of Na<sub>2</sub>SO<sub>3</sub> is then boiled with sulphur for two hours.

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

(b) It is prepared by dissolving NH<sub>4</sub>Cl in disodium hydrogen phosphate in molecular proportion in hot water.

(c) The conversion is made by Solvay process.

$$CO_2 + NH_3 + H_2O \longrightarrow NH_4HCO_3$$
  
 $NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$   
 $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$ 

(d) The solution of sodium sulphite is boiled with sulphur in an iron retort for two hours.

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

(e) Sodium is first converted into sodamide by passing dry ammonia gas over heated sodium.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2 \uparrow$$

The liquid sodamide is then dropped over red hot charcoal.

$$2NaNH_2 + C \longrightarrow Na_2CN_2 + 2H_2$$
 Sod. cyanamide

$$Na_2CN_2 + C \longrightarrow 2NaCN$$

**Example 5.** 'A' is a binary compound of a univalent metal. 1.422 g of 'A' reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid 'B', that forms a hydrated double salt 'C' with  $Al_2(SO_4)_3$ . Identify 'A', 'B' and 'C'. [I.I.T. 1994]

## Solution:

Since 'B' forms a hydrated double salt with  $Al_2(SO_4)_3$ . 'B' should be a sulphate of a monovalent metal, i.e.,  $M_2SO_4$ . As the sulphate  $(M_2SO_4)$  consists one sulphur atom per molecule, its molecular mass can be determined from the given data.

0.321 g of sulphur is present in 1.743 g of sulphate

32.1 g of sulphur is present in 
$$=\frac{1.743}{0.321} \times 32.1 = 174.3$$
 g

Thus, the molecular mass of the sulphate is 174.3. Let the atomic mass of the metal be x.

So 
$$2x + 32.1 + 64 = 174.3$$
  
 $2x = 174.3 - 96.1 = 78.2$   
 $x = 39.1$ 

Thus, 'B' is 
$$K_2SO_4$$
 and 'C' is  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$   
2 [Oxide] + S  $\longrightarrow K_2SO_4$ 

Thus, the oxide is  $KO_2$  (potassium superoxide). The given data supports that 'A' is  $KO_2$ .

**Example 6.** (i) An inorganic compound (A) is formed on passing a gas (B) through a concentrated liquor containing sodium sulphide and sodium sulphite.

- (ii) On adding (A) into dilute solution of silver nitrate, a white precipitate appears which quickly changes into a black coloured compound (C).
- (iii) On adding two or three drops of ferric chloride into the excess of solution of (A), a violet coloured compound (D) is formed. This colour disappears quickly.
- (iv) On adding a solution of (A) into the solution of cupric chloride, a white precipitate is first formed which dissolves on adding excess of (A) forming a compound (E).

Identify (A) to (E) and give the chemical equations for the reactions at steps (i) to (iv). [Roorkee 1996]

## Solution:

The reactions indicate that the compound (A) is sodium thiosulphate. It is formed in step (i) by passing gas (B) which is either  $I_2$  or  $SO_2$ .

**Example 7.** A white solid is either  $Na_2O$  or  $Na_2O_2$ . A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.

- (i) Identify the substance and explain with balanced equation.
- (ii) Explain what would happen to the red litmus if the white solid were the other compound. [I.I.T. 1999]

### Solution:

(i) A piece of red litmus turns white when dipped into aqueous solution of white solid indicates that the solution has bleaching action on litmus. This is due to the presence of hydrogen peroxide in solution which is formed by action of water on sodium peroxide. Thus, the white solid is Na<sub>2</sub>O<sub>2</sub>.

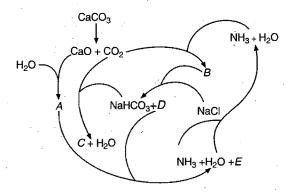
$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

(ii) The other compound is Na<sub>2</sub>O which gives NaOH (sodium hydroxide) with water.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

The solution, thus, turns red litmus to blue.

**Example 8.** The Solvay process can be represented by the following scheme:



Identify A, B, C, D and E.

[I.I.T. 1999]

## **Solution:**

 $(A): Ca(OH)_2$ 

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
(A)

 $(B): NH_4HCO_3$ 

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$
(B)

(C):  $Na_2CO_3$ 

$$2$$
NaHCO<sub>3</sub>  $\longrightarrow$  Na<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O + CO<sub>2</sub>

 $(D): NH_4Cl$ 

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$$
(D)

(E): CaCl<sub>2</sub>

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$$
(E)

**Example 9.** (a) Sodium fire in the laboratory should not be extinguished by pouring water. Why?

- (b) Alkali metals are paramagnetic but their salts are diamagnetic. Explain.
- (c) Why superoxides of alkali metals are paramagnetic while normal oxides are diamagnetic?

### **Solution**:

- (a) Sodium being highly electropositive element reacts vigorously with water evolving hydrogen which also catches fire. As a result, the fire spreads. Therefore, water should not be used to extinguish sodium fire.
- (b) Alkali metals possess ns<sup>1</sup> configuration, i.e., one unpaired electron is present and hence are paramagnetic. Alkali metals when form salts, the unpaired electron is transferred to the non-metallic atom forming anion. In salts, both cations and anions have paired electrons and hence, alkali metal salts are diamagnetic in nature.

(c) Superoxides contain the ion,  $O_2^-$  which has the following structure:

It has a three electron bond, *i.e.*, one unpaired electron is present and hence, is paramagnetic. Normal oxides contain the ion, O<sup>2-</sup>, which does not has unpaired electron and thus, are diamagnetic in nature.

**Example 10.** Comment on each of the following observations:

- (a) Lithium is the only alkali metal which forms nitride directly.
- (b) LiF is almost insoluble in water while LiCl is soluble in water as well as in acetone.
- (c) The mobilities of alkali metal ions in aqueous solutions are:

$$Li^+ < Na^+ < K^+ < Rb^+$$

## **Solution:**

(a) As it shows diagonal relationship with magnesium, it directly combines with nitrogen like magnesium and forms nitride.

$$6Li + N_2 \longrightarrow 2Li_3N$$

- (b) Lattice energy of LiF is very large as both Li<sup>+</sup> and F ions are small in size. Hence, LiF is almost insoluble in water. LiCl is partially covalent in nature due to polarisation of chloride ion by Li<sup>+</sup>. Thus, it is soluble in water as well as in acetone.
- (c) The degree of hydration is more for smaller ions. Thus, the mass of the hydrated ions follows the following order,

$$[\text{Li}(aq)]^+ > [\text{Na}(aq)]^+ > [\text{K}(aq)]^+ > [\text{Rb}(aq)]^+.$$

Therefore, the ionic mobility follows the following order:

$$[\text{Li}(aq)]^+ < [\text{Na}(aq)]^+ < [\text{K}(aq)]^+ < [\text{Rb}(aq)]^+$$

## •

## **SUMMARY AND IMPORTANT POINTS TO REMEMBER**



- 1. The group 1 or IA of the periodic table consists of six elements-lithium, sodium, potassium, rubidium, caesium and francium besides hydrogen. These elements are called alkali metals as the hydroxides of these elements are soluble in water and these solutions are highly alkaline in nature. Alkali is an Arabic word 'Alquili' meaning the ashes of plants from which compounds of sodium and potassium were first isolated.
- 2. The alkali metals are s-block elements as the last electron enters ns-orbital. They have [noble gas] ns<sup>1</sup> electronic configuration. The first member lithium, shows somewhat abnormal properties then rest of the members of the group as the penultimate shell in Li has two electrons while in rest of the alkali elements eight electrons are present in the penultimate shell.
- 3. The alkali metals, being reactive in nature, are never found free in nature but always found in combined state. Sodium and potassium are found in abundance as they are seventh and eighth most abundant elements by mass in earth's crust. The last member, francium, is radioactive and occurs only in traces as its half life is very small, *i.e.*, 21 minutes.
- 4. Except first period, rest of the six periods of the periodic table start with a member of alkali group. It is a most homogeneous group. The members of this group show a marked resemblance in their properties. There is a gradual gradation in the properties with the increase of atomic number.

## 5. Physical properties

(a) Alkali metals are soft with low melting and boiling points. This is due to weak intermetallic bonding. All are light metals having low densities. Densities increase from I to Cs with exception of K.

- (b) Alkali metals have the largest size in their respective periods. Atomic as well as ionic size increases as the at. no. increases from Li to Cs. At. volume also increases as the atomic number increases.
- (c) The ionisation energy decreases from Li to Cs as their size increases. They are highly electropositive, metallic in nature and reactivity increases from Li to Cs. All except lithium show photoelectric effect.
- (d) All alkali metals are paramagnetic but their salts are diamagnetic in nature. The alkali metals show only one oxidation state, *i.e.*, +1 in their compounds.
- (e) Alkali metals and their compounds impart characteristic colour to flame.

Li Na K Rb Cs Crimson red Golden yellow Pale violet Reddish violet Sky blue

- (f) The salts of alkali metals are ionic and soluble in water. The solubility is due to hydration of  $M^+$  ions. Smaller the ion, the greater is the degree of hydration. The degree of hydration decreases from Li<sup>+</sup> to Cs<sup>+</sup>. Consequently, the radii of the hydrated ion decreases from Li<sup>+</sup> to Cs<sup>+</sup>.
- (g) Due to large negative electrode potentials, alkali metals are strong reducing agents. The reducing nature increases from Na to Cs but Li is the strongest reducing agent as its reduction potential is highest, i.e, -3.05. This is due to large heat of hydration of Li<sup>+</sup> ion.
- (h) The alkali metals are good conductors of heat and electricity.

## 6. Chemical properties

The alkali metals are highly reactive elements. The reactivity is due to:

- (i) low value of ionisation energy
- (ii) low heat of atomisation.

The reactivity increases from Li to Cs. The compounds of alkali metals are electrovalent, colourless and soluble in water. These are crystalline solids. Lithium compounds show some abnormal properties due to polarisation on account of small size of Li<sup>+</sup> ion and high lattice energies.

- (a) On exposure to moist air, all alkali metals except lithium tarnish quickly. These are, therefore, always kept in kerosene to protect them from air.
- (b) Alkali metals decompose water with evolution of hydrogen. The reactivity towards water increases from Li to Cs. The decomposition is highly exothermic and the evolved hydrogen sometimes catches fire.
- (c) Alkali metals combine directly with hydrogen to form crystalline solids of formula MH. The hydrides react with water liberating hydrogen.
- (d) Affinity towards oxygen increases when heated in atmosphere of oxygen, the alkali metals ignite and form oxides.

The peroxides and superoxides become more stable with increase in atomic number of the alkali metal. The basic nature of the normal oxides increases gradually as the atomic number increases. The hydroxides (MOH) are thermally stable except LiOH. The relative strength of the hydroxides increases from LiOH to CsOH.

 $Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O$ LiOH < NaOH < KOH < RbOH < CsOH

Basic nature increases -----

The higher oxides, peroxides and superoxides are strong oxidising agents. They react with water and dilute acids forming H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>.

- (e) The alkali metals directly react with halogens forming halides (MX). With the exception of lithium halides, the alkali metal halides are ionic compounds. They are crystalline and have high melting and boiling points. The fused halides are good conductors of electricity. Alkali metal halides are colourless but on heating they turn yellow, blue, etc., due to crystal defects. Except LiF, all halides are soluble in water. The insolubility of LiF is due to high lattice energy. Halides of K, Rb and Cs have a property of combining with extra halogen atoms forming polyhalides.
- (f) Alkali metals directly combine with P and S when heated with them. Alkali metals, except lithium, do not combine directly with nitrogen.
- (g) All the alkali metals form carbonates of type  $M_2CO_3$ . Carbonates are stable towards heat and readily soluble in water. Li<sub>2</sub>CO<sub>3</sub> is an exception.

The aqueous solutions of carbonates are alkaline due to hydrolysis.

The bicarbonates (MHCO<sub>3</sub>) with the exception of LiHCO<sub>3</sub>, are known in solid state.

They are soluble in water and decompose on heating into corresponding carbonate with evolution of CO<sub>2</sub>.

- (h) Nitrates of the type, MNO<sub>3</sub>, are known. These are colour-less, soluble in water and electrovalent in nature. With the exception of LiNO<sub>3</sub>, the other nitrates decompose to nitrites and oxygen on heating. LiNO<sub>3</sub> decomposes to oxide with evolution of NO<sub>2</sub> and O<sub>2</sub>.
- (i) Sulphates of the type M<sub>2</sub>SO<sub>4</sub> are known with the exception of Li<sub>2</sub>SO<sub>4</sub>, other sulphates are soluble in water. Sulphates are reduced to corresponding sulphides when fused with carbon. Sulphates of alkali metals form double salts with the sulphates of trivalent metals like Fe, Al, Cr, etc.
- (j) The alkali metals dissolve in liquid ammonia without evolution of hydrogen. The colour of dilute solutions is blue. On heating colour changes to bronze. The colour is due to ammoniated electron.

 $M + (x + y) \text{ NH}_3 \longrightarrow [M(\text{NH}_3)_x]^+ + e(\text{NH}_3)_y$ These solutions are good conductors of electricity and have strong reducing properties. The solutions are paramagnetic in nature.

When dry ammonia is passed over hot metal, amides are formed.

7. The alkali metals form alloys amongst themselves and with other metals. These combine with mercury and form amalgams.

- **8.** Alkali metals have a very little tendency to form complexes. Lithium being small in size forms certain complexes but this tendency decreases as the size increases.
- 9. Alkali metals cannot be extracted by application of common processes used for the extraction of metals due to following reasons:
  - (i) Cannot be extracted by the reduction of their oxides and other compounds as being strong reducing agents.
  - (ii) Cannot be extracted by displacing them from their salt solutions by any other element as they are highly electropositive.
  - (iii) Cannot be extracted by electrolysis of the aqueous solutions of their salts as hydrogen is discharged at cathode instead of alkali metal.

The only successful method, therefore, is the electrolysis of their fused salts usually chlorides. Generally, another metal chloride is added to lower its fusion temperature.

- 10. Lithium shows abnormal properties due to its small size (atom and ion). Lithium ion on account of its small size exerts polarising effect on negative ions. Consequently, covalent character is developed in Li-salts. Li has highest ionisation energy and electronegativity as compared to other alkali metals.
  - (i) LiCl is more covalent than NaCl. LiCl is soluble in alcohol, pyridine, etc. Its melting point is lower than that of NaCl.
  - (ii) LiOH, Li<sub>2</sub>CO<sub>3</sub>, LiNO<sub>3</sub> behave differently than other alkali corresponding salts towards heating.

$$2\text{LiOH} \longrightarrow \text{Li}_2\text{O} + \text{H}_2\text{O}; \quad \text{Li}_2\text{CO}_3 \longrightarrow \text{Li}_2\text{O} + \text{CO}_2; 4\text{LiNO}_3 \longrightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$$

Hydroxides and carbonates of other alkali metals are stable. The nitrates of other alkali metals decompose giving only oxygen.

(iii) Lithium directly combines with nitrogen.

$$.6 \text{ Li} + \text{N}_2 \longrightarrow 2 \text{Li}_3 \text{N}$$

- (iv) LiHCO3 is known only in solution but not in solid state.
- (v) Li<sub>2</sub>SO<sub>4</sub> does not form double sulphates.
- (vi) LiF, Li<sub>3</sub>PO<sub>4</sub>, Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, Li<sub>2</sub>CO<sub>3</sub> are sparingly soluble in water.
- (vii) LiOH is weaker base in comparison to NaOH or KOH.
- (viii) Although Li has the highest ionisation potential, yet it is strongest reducing agent because of its large heat of hydration.
- 11. Lithium shows resemblance with magnesium, an element of group II A. This resemblance is termed diagonal relationship. The reasons for this resemblance are: (i) nearly same electronegativity (ii) not much difference in atomic size and ionic size (iii) nearly same atomic volumes (iv) nearly same polarising power.
- 12. Important minerals of sodium are: (i) chile saltpetre (NaNO<sub>3</sub>) (ii) Glauber's salt (Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O) (iii) trona (Na<sub>2</sub>CO<sub>3</sub>·2NaHCO<sub>3</sub>·3H<sub>2</sub>O) (iv) natron (Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O) (v) tincal or borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O) (vi) cryolite (Na<sub>3</sub>AlF<sub>6</sub>) (vii) soda felspar (NaAlSi<sub>3</sub>O<sub>8</sub>) (viii) common salt or rock salt or sea salt (NaCl).
- 13. Sodium is obtained on large scale by two processes.
  - (a) Castner's process: Electrolysis of fused sodium hydroxide is carried at 330°C using iron as cathode and nickel as anode. Hydrogen is discharged at cathode also.

(b) **Down's process:** Now-a-days, this process is applied. It involves electrolysis of fused NaCl to which CaCl<sub>2</sub> and KF have been added to reduce the melting point of NaCl. Iron is used as cathode and graphite as anode.

The electrolysis is carried at 600°C. Chlorine is discharged at anode.

- 14. Sodium is used in the manufacture of chemicals like Na<sub>2</sub>O<sub>2</sub> (oxone), sodamide, sodium cyanide, etc. It is used for making lead tetraethyl employed as antiknock in petrol. In molten state, it is used in nuclear reactors as heat transfer medium. For extraction of C, Be, Mg, Si, etc., in sodium lamps and as a laboratory reagent, sodium metal is also used.
- 15. The main source of NaCl is sea water which contains 2.7-2.9 % of the salt. Table salt becomes wet in rainy season due to presence of impurities of MgCl<sub>2</sub> and CaCl<sub>2</sub>.
- **16.** Sodium carbonate (washing soda), Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O, is generally prepared by a process called ammonia-soda process or Solvay process. The raw materials are NaCl, NH<sub>3</sub> and limestone.

$$NH_3 + H_2O + CO_2 \longrightarrow NIH_4HCO_3$$
 $NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$ 
 $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$ 

Solvay process cannot be employed for the manufacture of  $K_2CO_3$  because KHCO<sub>3</sub> is fairly soluble in water.

A mixture of NaHCO<sub>3</sub> and potassium hydrogen tartrate is called baking powder while sodium bicarbonate alone is called baking soda.

A mixture of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> is called fusion mixture. Anhydrous Na<sub>2</sub>CO<sub>3</sub> is called soda ash and obtained by heating Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O above 100°C. Sodium carbonate is used in laundries and in softening of water. It is used in the manufacture of glass, sodium silicate, borax, paper, soap powders, caustic soda, etc.

NaHCO<sub>3</sub> is used for making baking powder, in making effervescent drinks, in fire extinguishers and as a medicine.

- **17.** Sodium hydroxide (caustic soda) is manufactured on a very large scale by the following processes:
  - (i) Gossage process: Sodium carbonate reacts with suspension of lime (milk of lime or calcium hydroxide).

 $Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$ Calcium carbonate being insoluble separates out and the solution on evaporation gives flakes of caustic soda.

(ii) Lowig's process: A mixture of sodium carbonate and ferric oxide is heated to redness. Sodium ferrite is formed. The cooled sodium ferrite is thrown into hot water when hydrolysis occurs forming a solution of NaOH and insoluble ferric oxide.

$$Na_2CO_3 + Fe_2O_3 \longrightarrow 2NaFeO_2 + CO_2$$
  
 $2NaFeO_2 + H_2O \longrightarrow 2NaOH + Fe_2O_3$ 

- (iii) Electrolytic process: The electrolysis of sodium chloride is carried out in an electrolytic cell. The following electrolytic cells are used:
- (a) Nelson cell: It consists a perforated steel tube lined inside with asbestos. The tube acts as a cathode. A graphite rod dipped in sodium chloride solution serves as anode.
- **(b) Castner-Kellner cell:** This is a common cell in which mercury is used as cathode. The cell consists of a large

rectangular trough divided into three compartments by slate partitions. The mercury can flow from one compartment to other but the solution kept in one compartment cannot flow into other. Sodium chloride solution is kept in two outer compartments and a dilute solution of NaOH in the inner compartment. Two graphite electrodes which act as anodes are fitted in outer compartments and a series of iron rods fitted in the inner compartment act as cathode. Mercury in the outer compartments acts as cathode while in the inner compartment it acts as an anode by induction. The cell is kept rocking with the help of an eccentric wheel. Sodium discharged at the Hg cathode in the outer compartments forms amalgam which comes into the inner compartment due to rocking. Here, NaOH is formed.

(c) Keliner-Solvay cell: This is the modified cell having no compartments. Flowing Hg acts as cathode and a number of graphite rods act as anode in sodium chloride solution. The sodium amalgam flows out of cell and treated with water to form NaOH.

Commercial NaOH is purified with the help of alcohol. The alcoholic filtrate is distilled to get pure NaOH.

- 18. NaOH is a white crystalline solid. It has a soapy touch. It is highly deliquescent. It is highly soluble in water. It is a strong alkali. It cannot be kept in atmosphere as it absorbs moisture and CO<sub>2</sub>. It reacts with acids, acidic oxides and amphoteric oxides to form salts. It attacks non-metals like S, P, Si, B, halogens, etc. Metals like Zn, Al, Sn, Pb react with NaOH evolving H<sub>2</sub>. A number of metallic salts react with NaOH to form corresponding hydroxides. Ammonium salts evolve ammonia with NaOH. NaOH combines with CO under pressure to form sodium formate.
- 19. NaOH is used as a laboratory reagent, in manufacture of soap, in manufacture of paper and rayon, dyes and drugs. It is an absorber of gases. It is used in petroleum refining and for the manufacture of various useful sodium compounds.
- 20. Sodium peroxide (oxone), Na<sub>2</sub>O<sub>2</sub>, is formed by heating sodium at about 350°C in excess of air free from moisture. It is a pale yellow powder. It is used as an oxidising agent, for purification of air, for production of oxygen under the name oxone and for the preparation of H<sub>2</sub>O<sub>2</sub> and benzoyl peroxide.
- 21. Potassium is not found in the native state. In combined state it is widely distributed in nature. All plants contain considerable amount of potassium compounds. Its compounds

occur as salt beds in rocks and in sea water. The important minerals of potassium are :

Carnallite (KCl-MgCl<sub>2</sub>·6H<sub>2</sub>O), Indian saltpetre (KNO<sub>3</sub>), feldspar ( $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ ), sylvine (KCl), polyhalite ( $K_2SO_4 \cdot MgSO_4 \cdot CaSO_4 \cdot 6H_2O$ ), etc.

22. Potassium can be prepared by electrolysis of fused mixture of KCl and CaCl<sub>2</sub>. It is manufactured by reducing fluoride with calcium carbide at 1000°C.

$$2KF + CaC_2 \longrightarrow 2K + CaF_2 + 2C$$

Potassium is used in photoelectric cells. An alloy of potassium and sodium is used in special thermometers employed for measuring high temperatures.

23. Three oxides of potassium are known: (i) potassium monoxide, K<sub>2</sub>O (ii) potassium dioxide, KO<sub>2</sub> (iii) potassium sesquioxide, K<sub>2</sub>O<sub>3</sub>.

 $KO_2$  is prepared by burning potassium in excess of oxygen free from moisture. It is a chrome yellow powder. It dissolves in water giving  $H_2O_2$  and  $O_2$ . It is used as an oxidising agent, as air purifier in space capsules, submarines and breathing masks as it produces oxygen and removes  $CO_2$ .

KO<sub>2</sub> has bond order 1.5 and possesses paramagnetic nature due to the presence of one unpaired electron.

**24.** K<sub>2</sub>CO<sub>3</sub> is called potash or pearl ash. It is prepared by Le-Blanc process,

$$KCl \longrightarrow K_2SO_4 \xrightarrow{CaCO_3+C} K_2CO_3$$

it is used in the manufacture of hard glass.

KHCO<sub>3</sub> resembles NaHCO<sub>3</sub> in all respects except that it is more soluble in water. It is used in medicine and in baking powders.

- **25.** Caustic potash, KOH, is manufactured like NaOH, *i.e.*, by electrolysis of KCl. It is used for making soft soaps.
- Although both NaCN and KCN are poisonous but KCN is more poisonous than NaCN.
- 27. Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O is called Glauber's salt, anhydrous Na<sub>2</sub>SO<sub>4</sub> is called salt cake, NaHSO<sub>4</sub> is called nitre cake.
- **28.** Sodium thiosulphate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, is used as antichlor in bleaching.
- 29. Electric eye used in television contains an alloy of caesium and silver.
- **30.** All alkali metal azides are thermally unstable and liberate nitrogen and metal on heating. Lithium azide (LiN<sub>3</sub>) is an exception. It forms stable nitride on heating.

$$3\text{LiN}_3 \longrightarrow \text{Li}_3\text{N} + 4\text{N}_2$$

## ■ Subjective Type Questions

PRACTICE

## 1. Answer the following:

- (a) Why does table salt get wet in rainy season?
- (b) Which out of sodium or potassium has higher boiling point?
- (c) Why caesium is used in photoelectric cell while lithium cannot be?
- (d) What makes lithium to show properties different than other alkali metals?

#### 2. Give reasons:

- (a) LiCl is soluble in alcohol.
- (b) MgCl<sub>2</sub> is more covalent than NaCl.
- (c) LiBr has lower melting point than LiF.

## 3. Answer the following:

- (a) Name the alkali metals which form superoxides when heated in excess of air.
- (b) Which one is soluble in water?

(c) Which one is soluble in NaOH?

Al(OH)<sub>3</sub> or Fe(OH)<sub>3</sub>

- (d) Which alkali metal is radioactive in nature?
- (e) Name the alkali metal which shows diagonal relationship?
- (f) Which alkali metal is strongest reducing agent in aqueous solution.

## 4. Answer the following:

- (a) Which is the most abundant alkali metal in the earth's crust?
- (b) Which sodium salt is found in plenty in sea water?
- (c) Name one silicate and one phosphate ore of lithium.
- (d) Write the formulae of:
  - (i) Caustic potash (ii) Soda ash (iii) Chile saltpetre
- (e) Which compound of sodium is used for making baking powder?

## 5. Answer the following:

- (i) What is meant by black ash?
- (ii) What is the action of NaOH on ammonium salts?
- (iii) Which electrolyte is used to obtain sodium in Castner's process?
- (iv) What is washing soda?
- (v) Which electrolyte is used in Nelson's cell?
- (vi) What is the intermediate product in Solvay's process?
- (vii) Most abundant alkali metal in the earth's crust is :
- (viii) Which chloride of an alkali metal is soluble in alcohol?
- (ix) Which substance is added to sodium chloride as to reduce its fusion temperature during manufacture of sodium?
- (x) What product is formed when carbon monoxide is passed through sodium hydroxide under high pressure?
- **6.** What happens when following are heated?
  - (i) Potassium nitrate
- (ii) Sodium carbonate
- (iii) Microcosmic salt
- (iv) Sodium bicarbonate
- (v) Lithium hydroxide
- (vi) Lithium nitrate
- (vii) Lithium carbonate
- (viii) Sodium thiosulphate
- 7. What happens when?
  - (a) Hot and concentrated caustic soda solution reacts with iodine.
  - (b) White phosphorus is heated with caustic soda.
  - (c) Sodium thiosulphate is added to silver nitrate solution.
  - (d) Iodine is reacted with hypo solution.
  - (e) Excess of caustic soda reacts with zinc sulphate solution.
  - (f) Excess of NaOH is added to AlCl<sub>3</sub> solution.
  - (g) Anhydrous potassium nitrate is heated with excess of metallic potassium. [I.I.T. 1992]
  - (h) Copper sulphate reacts with potassium iodide.
  - (i) Copper sulphate is treated with hypo.
  - (j) Sodium is strongly heated in oxygen and the product is treated with H<sub>2</sub>SO<sub>4</sub>.
- 8. Complete and balance the following equations:
  - (i)  $KO_2 + H_2O \longrightarrow \dots + O_2$
  - (ii)  $NaNH_2 + C \longrightarrow \dots + H_2$
  - (iii)  $PbO_2 + NaOH \xrightarrow{Heat} \dots + H_2O$ (Conc.)

- (iv)  $KI + H_2SO_4 + H_2O_2 \longrightarrow I_2 + \dots + H_2O$
- (v) NaOH +  $I_2 \longrightarrow \dots + NaIO_3 + H_2O$ 9. Write the balanced equations of the reactions of:
  - (a) Caustic soda on the following:
    - (i) zinc, (ii) silver nitrate, (iii) phosphorus,
    - (iv) arsenious oxide
  - (b) Hypo on the following:
    - (i) FeCl<sub>3</sub>, (ii) AgCl, (iii) CuSO<sub>4</sub>, (iv) I<sub>2</sub>
- 10. Explain the following:
  - (i) Sodium is less reactive than potassium.
    - [**Hint**: Ionisation potential of potassium is less than sodium, *i.e.*, the tendency to lose valency electron is more in potassium than sodium.]
  - (ii) Alkali metals are paramagnetic but their salts are diamagnetic.
    - [Hint: In metals, the outermost energy shell is singly occupied but in cations, all the orbitals are doubly occupied (inert gas configuration).]
  - (iii) Sodium salts in aqueous solutions are either neutral or alkaline in nature.
    - [Hint: The anions in sodium salts are either from strong acids or weak acids. When anions from strong acids, there is no hydrolysis and aqueous solutions are neutral (NaCl soln.). On the other hand when anions from weak acids, there is hydrolysis of anions and the solutions are alkaline in nature (Na<sub>2</sub>CO<sub>3</sub> soln.).

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^{-} + OH^{-}$$
  
 $HCO_3^{-} + H_2O \rightleftharpoons H_2CO_3^{-} + OH^{-}$ 

- (iv) Standard solution of NaOH cannot be prepared by direct weighing.
  - [Hint: NaOH is affected by atmosphere. It absorbs moisture and CO<sub>2</sub> from atmosphere. Thus, accurate weighing of NaOH is not possible.]
- (v) Commercial common salt becomes slightly damp on keeping.
  - [Hint: Pure NaCl is not hygroscopic. The commercial common salt consists small amounts of magnesium chloride and calcium chloride which absorb moisture from atmosphere making it damp.]
- (vi) Sodium metal can be used for drying diethyl ether but not ethanol.
  - [Hint: Sodium metal reacts with ethanol,  $2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2$  and thus cannot be used for its drying.]
- (vii) A sodium fire in laboratory is not extinguished by water.
  - [Hint: Sodium reacts with water to produce hydrogen which is also inflammable. Pyrene (CCl<sub>4</sub>) can be used for this purpose.]
- (viii) The hydroxides of aluminium and iron are insoluble in water but NaOH is used to separate one from the other.

  [I.I.T. 1991]
  - [Hint: Al(OH)<sub>3</sub> dissolves in excess of NaOH forming a soluble compound, sodium meta aluminate.

    Al(OH)<sub>3</sub> + NaOH → NaAlO<sub>2</sub> + 2H<sub>2</sub>O]
- (ix) The inside surface of a glass bottle containing caustic soda becomes dull.

- [Hint: Silica is present in glass. It dissolves in NaOH slowly and forms soluble sodium silicate and thus inside surface becomes dull.]
- (x) Amongst LiF and LiI which has more covalent character and why?

[Hint: Lil is more covalent. According to Fajan's rule, Li+ will be able to polarise the bigger ion, I, more than the smaller ion, F-. More polarisation brings more covalent character.]

- 11. Give one test each to make distinction between the following pairs:
  - (i) NH<sub>4</sub>Cl and KCl
- (ii) Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>
- (iii) Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (iv) KNO<sub>3</sub> and KI
- (v) Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> (vi) NaCl and KCl
- 12. Arrange the following as specified:
  - (i) MgO, SrO, K2O, NiO and Cs2O (increasing order of basic character) [I.I.T. 1991]
  - (ii) LiCl, LiBr and LiI (decreasing order of covalent character)
  - (iii) KCl, KBr and KI (decreasing solubility in water)
  - (iv) NaHCO<sub>3</sub>, KHCO<sub>3</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub> and Ca(HCO<sub>3</sub>)<sub>2</sub> (increasing solubility)
  - (v) LiF, NaF, KF, RbF and CsF (in order of increasing lattice
  - (vi) Li, Na and K (in order of decreasing reducing nature in solution)
- 13. Identify (A), (B), (C) and (D) and give their chemical formulae.

$$(A) + \text{NaOH} \xrightarrow{\text{Heat}} \text{NaCl} + \text{NH}_3 + \text{H}_2\text{O}$$

$$\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \longrightarrow (B)$$

$$(B) + \text{NaCl} \longrightarrow (C) + \text{NH}_4\text{Cl}$$

$$(C) \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + (D)$$

14. From the reactions given below, identify (A), (B), (C) and (D)and give their formulae.

$$(A)_{(aq.)} + \operatorname{Zn} \longrightarrow (B)_{\operatorname{gas}}$$

$$(A)_{(aq.)} + (C) \xrightarrow{\operatorname{Heat}} \operatorname{PH}_{3}$$

$$(A)_{(aq.)} + \operatorname{NH}_{4}\operatorname{Cl} \longrightarrow (D)_{\operatorname{gas}}$$

- 15. A certain compound (X) imparts a golden yellow flame and shows the following reactions:
  - (i) Zinc powder when boiled with a concentrated solution of (X) dissolves and hydrogen is evolved.
  - (ii) When an aqueous solution of (X) is added to an aqueous solution of stannous chloride, a white precipitate is obtained first which dissolves in excess of solution of (X).

Identify (X) and write equations for reactions at steps (i) and (ii). [Roorkee 1991]

- **16.** A certain compound (X) is used in the laboratory for analysis, its aqueous solution gives the following reactions:
  - (i) On addition to copper sulphate, a brown precipitate is obtained which turns white on addition of excess of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.

(ii) On addition of Ag+ ion solution, a yellow curdy precipitate is obtained which is insoluble in ammonium hydroxide.

Identify (X) and give equations for the reactions at steps (i)and (ii). [Roorkee 1991]

- 17. An unknown inorganic compound (X) loses its water of crystallization on heating and its aqueous solution gives the following reactions:
  - (a) It gives a white turbidity with dilute HCl solution.
  - (b) It decolourises a solution of iodine in potassium iodide.
  - (c) It gives a white precipitate with silver nitrate solution which turns black on standing.

Identify the compound (X) and give chemical equations for the reactions at steps (a), (b) and (c).

- 18. When 20.02 g of a white solid X is heated, 4.4 g of an acid gas (A) and 1.8 g of a neutral gas (B) are evolved, leaving behind a solid residue (Y) of weight 13.8 g. (A) turns lime water milky and (B) condenses into liquid which changes anhydrous copper sulphate blue. The aqueous solution-of (Y) is alkaline to litmus and gives 19.7 g white precipitate (Z)with barium chloride solution. (Z) gives carbon dioxide with an acid. Identify A, B, X, Y and Z.
- 19. When 16.78 g of a white solid X were heated, 4.4 g of acid gas A that turned lime water milky was driven off together with 1.8 g of a gas B which condensed to a colourless liquid. The solid that remained, Y, dissolved in water to give an alkaline solution, which with excess of barium chloride solution gave a white precipitate, Z. The precipitate effervesced with acid giving off carbon dioxide. Identify A, B and Y and write down the equation for the thermal decomposition of X.
- Gradual addition of potassium iodide solution to Bi(NO<sub>3</sub>)<sub>3</sub> solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write the chemical equations for the above reactions. [L.I.T. 1996]

## Matching Type Questions

## Match the following:

[A]

- (a) Chile saltpetre
- (b) Indian saltpetre
- (c) Germicide
- (d) Baking soda
- (e) Washing soda
- (f) Hypo
- (g) Glauber's salt
- (h) Microcosmic salt
- (i) NaCN
- (ii) Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O
- (iii) Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O
- (iv) Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>
- (v) NaNH<sub>4</sub>HPO<sub>4</sub>·4H<sub>2</sub>O
- (vi) KNO<sub>3</sub>
- (vii) NaHCO<sub>3</sub>
- (viii) NaNO<sub>3</sub>

- B
- (a) Castner's process
- (b) Solvay process
- (c) Nelson's cell
- (d) Oxone
- (e) Pearl ash
- (f) Rock salt
- (g) Soda lime
- (h) Sylvine

- (i) KCl
- Potassium carbonate
- (iii) Sodium chloride
- (iv) Mixture (NaOH + CaO)
- (v) Sodium
- Sodium peroxide (vi)
- (vii) Sodium hydroxide
- (viii) Sodium carbonate

## Auswers

## Answers: Subjective Type Questions

- (a) Table salt contains impurities such as Na<sub>2</sub>SO<sub>4</sub>, CaSO<sub>4</sub>, MgCl<sub>2</sub> and CaCl<sub>2</sub>. These being hygroscopic absorb moisture from atmosphere. As a result, table salt gets wet.
  - (b) The melting point of sodium is higher as it has greater metallic bonding than potassium.
  - (c) Caesium has low ionisation enthalpy in comparison to lithium. Caesium can lose electrons very easily.
  - (d) Lithium shows different properties than other alkali metals due to following reasons:
    - (i) small atomic and ionic size
    - (ii) high ionisation potential
    - (iii) high polarizing power
- (a) Li<sup>+</sup> ion, being small in size, has high polarising power and hence LiCl is a covalent compound and thus, it is soluble in alcohol.
  - (b) Mg<sup>2+</sup> ion, on account of higher charge than Na<sup>+</sup> ion, has greater polarising power. Hence, MgCl<sub>2</sub> is more covalent than NaCl.
  - (c) Br ion, on account of bigger size than F ion, is more polarisable than F ion. Hence, LiBr is more covalent than LiF and thus, it has lower melting point.
- 3. (a) K, Rb, Cs (b) KF (c) Al(OH)<sub>3</sub> (d) Fr (e) Li (f) Li
- (a) sodium (b) sodium chloride (c) Lepidolite (silicate ore),
   Triphylite (phosphate ore) (d) (i) KOH (ii) Na<sub>2</sub>CO<sub>3</sub>
   (iii) NaNO<sub>3</sub> (e) NaHCO<sub>3</sub>
- 5. (i) Black ash is impure sodium carbonate produced in Le-Blanc method when salt cake is reduced by coke. (ii) Ammonia is liberated: NH<sub>4</sub>Cl + NaOH NH<sub>3</sub> + NaCl + H<sub>2</sub>O (iii) Fused sodium hydroxide. (iv) Sodium carbonate decahydrate. (v) Sodium chloride solution. (vi) Sodium bicarbonate. (vii) Sodium. (viii) Lithium chloride. (ix) Calcium chloride. (x) Sodium formate.
- **6.** (i)  $2KNO_3 \longrightarrow 2KNO_2 + O_2$ 
  - (ii) Water of crystallisation is lost and the substance becomes anhydrous,

- (viii)  $4Na_2S_2O_3 \longrightarrow 3Na_2SO_4 + Na_2S_5$
- 7. (a)  $6\text{NaOH} + 3\text{I}_2 \longrightarrow 5\text{NaI} + \text{NaIO}_3 + 3\text{H}_2\text{O}$ 
  - (b)  $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$
  - (c)  $2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$  $Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$
  - (d)  $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$
  - (e)  $ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2 + Na_2SO_4$
  - $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$
  - (f)  $AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$
  - $Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$
  - (g)  $2KNO_3 + 10K \longrightarrow 6K_2O + N_2$
  - (h)  $CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4$  $2CuI_2 \longrightarrow Cu_2I_2 + I_2$

(i) 
$$\text{CuSO}_4 + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{CuS}_2\text{O}_3 + \text{Na}_2\text{SO}_4$$
  
 $2\text{CuS}_2\text{O}_3 + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Cu}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{S}_4\text{O}_6$   
 $3\text{Cu}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_4[\text{Cu}_6(\text{S}_2\text{O}_3)_5]$ 

$$\begin{array}{ccc} \text{(j)} & & 2\text{Na} + \text{O}_2 \xrightarrow{\text{Heat}} \text{Na}_2\text{O}_2 \\ & & \text{Na}_2\text{O}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}_2 \end{array}$$

8. (i) 
$$4KO_2 + 2H_2O \longrightarrow 4KOH + 3O_2$$

(ii) 
$$2\text{NaNH}_2 + C \xrightarrow{\text{Heat}} \text{Na}_2\text{CN}_2 + 2\text{H}_2 \uparrow$$
  $\text{Na}_2\text{CN}_2 + C \longrightarrow 2\text{NaCN}$ 

- (iii)  $PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$
- (iv)  $2KI + H_2SO_4 + H_2O_2 \longrightarrow I_2 + K_2SO_4 + 2H_2O_4$
- (v)  $6\text{NaOH} + 3\text{I}_2 \longrightarrow 5\text{NaI} + \text{NaIO}_3 + 3\text{H}_2\text{O}$
- 9. (a) See properties of NaOH.
  - (b) See properties of sodium thiosulphate.
- 11. (a) When heated with NaOH, NH<sub>4</sub>Cl evolves ammonia gas.

$$NH_4Cl + NaOH \longrightarrow NH_3 + NaCl + H_2O$$

(b) On treatment with dil. H<sub>2</sub>SO<sub>4</sub>, a pungent gas, SO<sub>2</sub>, is evolved which turns acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> green.

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2$$

(c) On addition of AgNO<sub>3</sub> solution, sodium thiosulphate gives a white precipitate which turns black.

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$$
  
 $Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$ 

(d) On addition of AgNO<sub>3</sub> solution, KI gives a yellow precipitate of AgI.

$$2AgNO_3 + 2KI \longrightarrow 2AgI + 2KNO_3$$

- (e) On addition of dil. HCl, Na<sub>2</sub>SO<sub>3</sub> gives pungent gas which turns acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> paper green.
- (f) Flame test.
- 12. (i) NiO < MgO < SrO <  $K_2O$  <  $Cs_2O$ 
  - (ii) LiI > LiBr > LiCl
  - (iii) KI > KBr > KCl, lattice energy of KI is lower than the lattice energy of KCl.
  - (iv)  $NaHCO_3 < KHCO_3 < Mg(HCO_3)_2 < Ca(HCO_3)_2$
  - (v) CsF < RbF < KF < NaF < LiF
  - (vi) Li > K > Na
- 13. (A) NH<sub>4</sub>Cl, ammonium chloride; (B) NH<sub>4</sub>HCO<sub>3</sub>, ammonium bicarbonate; (C) NaHCO<sub>3</sub>, sodium bicarbonate; (D) CO<sub>2</sub>, carbon dioxide.
- 14. (A) NaOH, sodium hydroxide; (B) H<sub>2</sub>, hydrogen; (C) P<sub>4</sub>, phosphorus; (D) NH<sub>3</sub>, ammonia.
- 15. (X) = NaOH

(i) 
$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$
  
(ii)  $SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$   
 $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$ 

Soluble

16. 
$$X = KI$$
  
(i)  $2CuSO_4 + 4KI \longrightarrow 2CuI_2 + 2K_2SO_4$   
 $2CuI_2 \longrightarrow Cu_2I_2 + I_2$   
(White)  $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$   
(ii)  $Ag^+ + KI \longrightarrow AgI + K^+$   
Yellow ppt.  
Insoluble in NH<sub>4</sub>OH

17.  $X = Na_2S_2O_3.5H_2O$ .

(a) 
$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2O + S + SO_2$$

(b) 
$$KI_3 + 2Na_2S_2O_3 \longrightarrow KI + 2NaI + Na_2S_4O_6$$

(c) 
$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$$
  
 $Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$ 

18. 
$$(X)$$

White solid

Acid gas

Neutral gas

Residue

20.02 g

4.4 g

1.8 g

13.8 g

H<sub>2</sub>O

Anhydrous

CuSO<sub>4</sub>

Alkaline to litmus

CuSO<sub>4</sub>·5H<sub>2</sub>O (Blue)

 $\downarrow$  BaCl<sub>2</sub> soln. White ppt. (Z) 19.7 g

 $CO_2 \stackrel{Acid}{\longleftarrow}$ 

(Z) is a carbonate as it evolves  $CO_2$  with acid. (Y) is also a carbonate of an alkali metal because its solution is alkaline to litmus and gives a white precipitate of  $BaCO_3$  with  $BaCl_2$  soln. (B) is  $H_2O$  and (A) is  $CO_2$ . Thus, (X) is a bicarbonate, MHCO<sub>3</sub>.

$$2MHCO_3 \longrightarrow CO_2 + H_2O + M_2CO_3$$

$$(X) \qquad (A) \qquad (B) \qquad (Y)$$

$$2[X + 61]$$

44 g  $CO_2$  is obtained from 2(X + 61) g of X

4.4 g CO<sub>2</sub> is obtained from 
$$\frac{2(X + 61)}{44} \times 4.4 = \frac{X + 61}{5}$$
 g of X

So, 
$$\frac{X+61}{5} = 20.02$$
 or  $X = 39.1$  g

Therefore, the alkali metal is K.

Thus, X is KHCO<sub>3</sub>

$$2KHCO_3 \longrightarrow K_2CO_3 + CO_2 + H_2O \\ (X) \qquad (Y) \qquad (A) \qquad (B)$$
 
$$K_2CO_3 + BaCl_2 \longrightarrow BaCO_3 + 2KCl$$

138.2 g of K<sub>2</sub>CO<sub>3</sub> forms 197 g BaCO<sub>3</sub>

13.8 g of  $K_2CO_3$  forms  $\frac{197}{138.2} \times 13.8$  g BaCO $_3$  or 19.7 g

This confirms the given data.

19. X is NaHCO<sub>3</sub>.

20. At first, Bi(NO<sub>3</sub>)<sub>3</sub> undergoes hydrolysis. Nitric acid is formed. Which oxidises KI to iodine. The liberated iodine dissolves in KI to form yellow solution of KI<sub>3</sub>.

$$\begin{array}{c} \text{Bi}(\text{NO}_3)_3 \ + \ \text{H}_2\text{O} \longrightarrow [\text{Bi}(\text{OH})(\text{NO}_3)_2] \ + \ \text{HNO}_3 \\ \\ 2\text{HNO}_3 \longrightarrow \text{H}_2\text{O} \ + \ 2\text{NO}_2 \ + \ \text{O} \\ \\ 2\text{KI} \ + \ \text{H}_2\text{O} \ + \ \text{O} \longrightarrow 2\text{KOH} \quad + \quad \text{I}_2 \\ \\ \text{Dark brown} \\ \\ \text{I}_2 \ + \ \text{KI} \longrightarrow \qquad \text{KI}_3 \\ \text{Yellow solution} \end{array}$$

Answers: Matching Type Questions

- [A] (a—viii); (b—vi); (c—i); (d—vii); (e—ii); (f—iv); (g—iii); (h—v);
- [B] (a—v); (b—viii); (c—vii); (d—vi); (e—ii); (f—iii); (g—iv); (h—i)

## ILLUSTRATIONS OF OBJECTIVE QUESTIONS



- 1. Which one of the following statements is true for all the alkali metals?
  - (a) Their nitrates decompose on heating to give  $NO_2$  and  $O_2$ .
  - (b) Their carbonates decompose on heating to give CO<sub>2</sub> and normal oxide.
  - (c) They react with halogens to give the halides of the type, MX.
  - (d) They react with oxygen to give mainly the oxide,  $M_2$ O. Ans. (c)
- 2. The electrolyte used in Castner's process of sodium extraction is:
  - (a) anhydrous Na<sub>2</sub>CO<sub>3</sub>
- (b) aqueous NaOH
- (c) NaCl + CaCl<sub>2</sub>
- (d) fused anhydrous NaOH

Ans. (d)

- 3. Based on lattice energy and other considerations which one of the following alkali metal chloride is expected to have highest melting point?
  - (a) LiCl

(b) NaCl

(c) KCl

(d) RbCl

Ans. (b)

[Hint: On the basis of lattice energy, the melting point decreases in the alkali group as lattice energy decreases with the

increase of the atomic number. However, LiCl has covalent character due to very small size of Li<sup>+</sup> ion. Hence, melting point of NaCl is highest amongst the above chlorides.]

- 4. Select correct statement:
  - (a) Oxides  $(M_2O)$  and peroxides  $(M_2O_2)$  of alkali metals are diamagnetic and colourless.
  - (b) Superoxides  $(MO_2)$  of alkali metals are paramagnetic.
  - (c) Li and Na do not form superoxides.
  - (d) All are correct.

Ans. (d)

- 5. Which of the following salts does not form any precipitate with excess of NaOH?
  - (a) ZnCl<sub>2</sub>
- (b) FeCl<sub>3</sub>
- (c) CrCl<sub>3</sub>
- (d) CuSO<sub>4</sub>

Ans. (a)  $[\text{Hint}: ZnCl_2 + NaOH \longrightarrow Zn(OH)_2 \xrightarrow{\text{NaOH}} Na_2ZnO_2$ Soluble

 $FeCl_3 + NaOH \longrightarrow Fe(OH)_3$  (brown ppt.)

 $CrCl_3 + NaOH \longrightarrow Cr(OH)_3$  (green ppt.)

 $CuSO_4 + NaOH \longrightarrow Cu(OH)_2$  (blue ppt.)]

**6.** Which of the following is best CO<sub>2</sub> absorber as well as source of O<sub>2</sub> in space capsule?

(a)	$KO_2$
(c)	KOH
An	s. (a)

(b)  $K_2O_2$ 

(d) LiOH

[Hint:  $4KO_2 + 2CO_2 \longrightarrow 2K_2CO_3 + 3O_2$ ]

Match the compounds given in (X) with their uses in (Y).

(Y)

- A. NaOH
- Glass 1.
- B. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>
- 2. Germicide
- C. NaCN
- 3. Antichlor

D. Na<sub>2</sub>CO<sub>3</sub>

Soap

## Codes:

	Α	В	C	D
(a)	4	3	2	1
(b)	3	4	- 1	2
(c)	2	3	4	. 1
(d)	1	2	3	4

- Ans. (a)
- 8. On dissolving moderate amount of sodium metal in liquid ammonia at low temperature, which of the following does not occur?
  - (a) Blue coloured solution is obtained
  - (b) Na<sup>+</sup> ions are formed in solution
  - (c) Liquid ammonia becomes good conductor of electricity
  - (d) The liquid ammonia remains diamagnetic Ans. (d)
- The aqueous solutions of lithium salts are poor conductor of electricity rather than other alkali metals because of:
  - (a) high ionisation energy
  - (b) high electronegativity
  - (c) lower ability of Li<sup>+</sup> ions to polarise water molecules
  - (d) higher degree of hydration of Li<sup>+</sup> ions Ans. (d)
- 10. NaOH + CO $\xrightarrow{200^{\circ}\text{C}} X$ . The product X is :
  - (a) NaHCO<sub>3</sub>
- (b) Na<sub>2</sub>CO<sub>3</sub>
- (c) HCOONa
- (d)  $H_2CO_3$

- Ans. (c)
- 11. Which of the property of alkali metals is not listed correctly?
  - (a) The least electronegative metal: Cs
  - (b) A natural radioactive metal: Fr
  - (c) The alkali metal with lowest density: K
  - (d) The most abundant alkali metal in earth's crust : Na Ans. (c)

- 12. Which among the following is least soluble in water?
  - (a) NaF

(b) LiF

(c) KF

(d) RbF

Ans. (b)

[Hint: LiF has maximum lattice energy and hence least soluble.]

- 13. Which of the following metals is used for drying organic solvents?
  - (a) Magnesium
- (b) Sodium
- (c) Platinum
- (d) Nickel

Ans. (b)

- 14. Which of the following does not illustrate the anomalous behaviour of lithium?
  - (a) Lithium reacts with nitrogen to form a nitride
  - (b) Lithium is the hardest alkali metal
  - (c) Lithium reacts with oxygen to form normal oxide only
  - (d) Lithium carbonate decomposes on heating Ans. (b)
- 15. The correct order of stability of hydrides of alkali metals is:
  - (a) LiH > NaH > KH > RbH (b) NaH > KH > RbH > LiH
  - (c) RbH > KH > NaH > LiH (d) LiH > RbH > KH > NaH Ans : (a)

[Hint: Small anion forms stable compound with small cation.]

- 16. The correct order of mobility of alkali metal ions in aqueous solution is: [C.B.S.E. 2006]
  - (a)  $K^+ > Rb^+ > Na^+ > Li^+$
- (b)  $Rb^+ > K^+ > Na^+ > Li^+$
- (c)  $Li^+ > Na^+ > K^+ > Rb^+$
- (d)  $Na^+ > K^+ > Rb^+ > Li^+$

Ans : (b)

[Hint: Smaller the size of the ion, more is the hydration and therefore lesser is the mobility.]

- 17. Pick out statement(s) which is(are) not true about diagonal relationship of Li and Mg:
  - A Polarising powers of Li<sup>+</sup> and Mg<sup>2+</sup> ions are almost same
  - B Like Li, Mg decomposes water very fast
  - C LiCl and MgCl<sub>2</sub> are deliquescent
  - D Like Li, Mg readily reacts with liquid bromine at ordinary temperature
  - (a) A and D
- (b) B and C
- (c) Only B Ans : (d)
- (d) B and D

# **OBJECTIVE QUESTIONS**



Set I: Choose the correct answer out of the given alternatives for each question.

1.	Electrometallurgical process (e is employed to extract:	electrolysis of fused electroly	yte)	13.	The colour of iodine solutaqueous solution of:	ion is	discharged by shaking it	with
	(a) iron	(b) lead		.*	(a) $H_2SO_4$		(b) sodium sulphide	
	(c) silver	(d) sodium			· · · · ·		(d) sodium thiosulphate	
2.	Molecular formula of Glauber		-	14.	Which of the following i			
		(b) CuSO <sub>4</sub> ·5H <sub>2</sub> O			(a) LiHCO <sub>3</sub>		(b) NaHCO <sub>3</sub>	
	-	- · · ·			(c) KHCO <sub>3</sub>		(d) NH <sub>4</sub> HCO <sub>3</sub>	
2		(d) FeSO <sub>4</sub> ·7H <sub>2</sub> O		15.	Sodium metal can be stor			
3.	Nitrogen dioxide cannot be o				(a) benzene		(b) kerosene	
	` '	(b) Pb(NO <sub>3</sub> ) <sub>2</sub>			(c) alcohol		(d) water	
1		(d) AgNO <sub>3</sub>		16.	A substance X is a comp		• •	IA.
4.	An ingredient of baking power	(b) Na <sub>2</sub> CO <sub>3</sub>			The substance X gives a		0 1	
	(a) NaHCO <sub>3</sub>	(d) NaCl			(a) NaCl		(b) LiCl	
5	V-2	, ,			(c) KCl		(d) None of these	
J.	Sodium reacts with water r because:	note vigorousty than hun	iuiii	17.	Select the correct stateme		•	
	(a) it has higher atomic mass	•			(a) Lithium carbonate is		le in water	
	(b) it is more electropositive	I			(b) Potassium carbonate	is sol	uble in water	
	(c) it is more electronegative				(c) Barium carbonate is s	olubl	e in water	
	(d) it is a metal				(d) Bicarbonate of lithiur	n is ir	nsoluble in water	
6.	Washing soda is:		LJ	18.	Alkali metals are powerf	ul red	lucing agents because:	
U.	(a) Na <sub>2</sub> CO <sub>3</sub>	(b) Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O			(a) these are metals			
	(c) KHCO <sub>3</sub>				(b) these are monovalent	t		
7.	On heating sodium carbonate	. ,		ĺ	(c) their ionic radii are la	rge		
	(a) CO <sub>2</sub>	(b) CO			(d) their ionization poten			
	(c) H <sub>2</sub> O	(d) NO gas		19.	Sodium carbonate is prep	pared	by:	
8.	Sodium carbonate can be ma	- · · · -			(a) Solvay process		(b) Kolbe's process	
٠.	but potassium carbonate can				(c) Contact process		(d) Nessler's process	
	(a) K <sub>2</sub> CO <sub>3</sub> is more soluble			20.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O is used in	n phot	tography to:	
	(b) K <sub>2</sub> CO <sub>3</sub> is less soluble				(a) reduce AgBr to metal	lic Ag	g	
		han NaUCO			(b) remove reduced Ag			
	(c) KHCO <sub>3</sub> is more soluble the				(c) remove undecompose	d Ag	Br as a soluble complex	
	(d) KHCO <sub>3</sub> is less soluble the				(d) convert metallic Ag t			
9.	Which of the following repres	ems correct order of decreas	sing	21.	The reaction of sodium t			
	$E_{ox}^{o}$ or reducing nature? (a) Li > Na > K > Rb	(b) Rb > K > Na > Li			(a) sodium sulphide		(b) sodium sulphite	
		(d) $\text{Li} > \text{Rb} > \text{K} > \text{Na}$			(c) sodium sulphate		(d) sodium tetrathionate	
10	The solubility of $MClO_4$ ( $M =$	* *		22.	,			
10.	of:	Li, iva, ix, ixoy mercuses in o	iuci		(a) Na		(b) NaOH	
	(a) LiClO <sub>4</sub> < NaClO <sub>4</sub> < KClO	L < RhClO			(c) NaClO		(d) NaClO <sub>3</sub>	
	(b) NaClO <sub>4</sub> < RbClO <sub>4</sub> < LiClO	•		23.		of so	odium hydroxide solutio	n to
	(c) RbClO <sub>4</sub> < KClO <sub>4</sub> < NaClO				form: ,		4) N. G.O.	
	(d) KClO <sub>4</sub> < LiClO <sub>4</sub> < NaClO				(a) $Sn(OH)_2$		(b) $Na_2SnO_3$	니
11.					(c) $Na_2SnO_2$		(d) $SnO_2$	
	(a) good conductors of heat	•		24.	The hydroxide of which		al ion is soluble in exces	ss of
	(b) high melting points				sodium hydroxide solution	on:		
	(c) low oxidation potentials				(a) Fe <sup>+++</sup>		(b) Cr <sup>+++</sup>	
	(d) high ionisation potential	S			(c) Al <sup>+++</sup>		(d) Cu <sup>++</sup>	
12.				25.	An element having elec	tronic	c configuration $1s^2$ , $2s^2$	$2p^{6}$ ,
	due to the presence of:		U		$3s^2 3p^6$ , $4s^1$ will form:		-	_
	(a) sodium atoms	(b) sodium hydride			(a) acidic oxide		(b) basic oxide	
	(c) sodium amide	(d) solvated electrons			(c) amphoteric oxide		(d) neutral oxide	
					=			

26.	The products of electrolysis of concentrated common solution are:	salt	38.	Na <sub>2</sub> CO <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> $\longrightarrow$ A + CO <sub>2</sub> , what is A in the reaction? (a) NaFeO <sub>2</sub> $\square$ (b) Na <sub>3</sub> FeO <sub>3</sub> $\square$
				(c) $Fe_3O_4$
	(a) $Na + Cl_2$		20	· / 2 2
	(c) NaOH + $H_2$ + $Cl_2$ $\Box$ (d) NaOH + $Cl_2$ + $O_2$		39.	When dry ammonia gas is passed over heated sodium (out
27.	Elements in the first column of the periodic table are c	alled		of contact of air) the product formed is:
	alkali metals. These metals have:	* .		(a) sodium hydride
	(a) a single valency electron			(c) sodamide $\Box$ (d) sodium cynamide $\Box$
	(b) one electron less than an inert gas configuration		40.	The name oxone is given to:
	(c) high melting points			(a) ozone $\Box$ (b) sodium peroxide $\Box$
	(d) high ionisation potentials			(c) sodium oxide $\Box$ (d) sodamide $\Box$
28.	One of the natural minerals of sodium is tincal. Its for	mula	41.	The principal products obtained on heating iodine with
	is:			concentrated caustic soda solution:
	(a) Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O			(a) NaIO + NaI
	(c) $Na_2B_4O_7:10H_2O$ $\square$ (d) $NaCl$			(c) $NaIO_3 + NaI$ $\square$ (d) $NaIO_4 + NaI$ $\square$
29	Potassium when heated strongly in oxygen, it forms:	_	42.	When a concentrated solution of ammonia is saturated with
2).	(a) $K_2O$ $\Box$ (b) $KO_2$			sodium chloride in the presence of pieces of dry ice, a water
	(c) $K_2O_2$ $\square$ (d) $KO_2$			cloud is formed. This is due to :
20	*			(a) precipitation of sodium hydrogen carbonate from the
30.	The reaction of sodium is highly exothermic with water	. 1116		reaction mixture
	rate of reaction is lowered by:			(b) precipitation of ammonium carbonate
	(a) lowering the temperature			(c) precipitation of ammonium hydrogen carbonate from the
	(b) mixing with alcohol			
	(c) mixing with acetic acid			reaction mixture
	(d) making an amalgam			(d) precipitation of sodium carbonate from the reaction
31.	What product is obtained after electrolysis in Solvay tr	rough		mixture
	cell ?			[Hint: $NH_3 + H_2O + CO_2$ (dry ice) $\longrightarrow NH_4HCO_3$
	(a) NaOH			$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl]$
	(c) Na $\Box$ (d) Na <sub>2</sub> CO <sub>3</sub>		43.	A combustible gas is liberated when caustic soda solution
32.	RbO <sub>2</sub> is:			is heated with:
	(a) superoxide and paramagnetic	· 🗆		(a) S $\square$ (b) NH <sub>4</sub> Cl $\square$
•	(b) superoxide and diamagnetic			(c) $I_2$ $\square$ (d) $Z_n$
	(c) peroxide and paramagnetic		44.	Caustic soda is:
	(d) peroxide and diamagnetic			(a) efflorescent $\Box$ (b) deliquescent $\Box$
33.	KOH is preferably used to absorb CO <sub>2</sub> gas because:	`		(c) hygroscopic $\Box$ (d) oxidant $\Box$
	(a) KHCO <sub>3</sub> is soluble in water while NaHCO <sub>3</sub> is spar	ringly	45.	When ammonical common salt solution is saturated with
	soluble in water	Ő		carbon dioxide we obtain:
	(b) KOH is cheaper than NaOH			(a) $NH_4HCO_3$
	(c) KOH is stronger base than NaOH			(c) NaHCO <sub>3</sub>
	(d) KOH is more soluble than NaOH in water		46.	The compound called microcosmic salt is:
34.	What are the raw materials used in Solvay process?	-		(a) $Na_2HPO_4\cdot 2H_2O$ $\square$ (b) $Na(NH_4)HPO_4\cdot 4H_2O$ $\square$
51.	(a) NaCl, NH <sub>3</sub> , CaCO <sub>3</sub>			(c) $Na_2NH_4PO_4\cdot 2H_2O$ $\square$ (d) $(NH_4)_2HPO_4\cdot 2H_2O$ $\square$
	(c) NaCl, $CO_2$		47.	From a solution of zinc chloride, zinc carbonate can be
	(d) NaCl, CaCO <sub>3</sub> , C, H <sub>2</sub> SO <sub>4</sub>		"	obtained by adding:
25		<u></u>		(a) NaHCO <sub>3</sub>
35.	The solubility of iodine in water is increased by:	П		(c) $CaCO_3$
	(a) boiling the solution		48.	Sodium carbonate solution is alkaline due to:
	(b) cooling the solution		70.	(a) hydrolysis of Na <sup>+</sup>
	(c) adding acid			
	(d) adding potassium iodide			(-))
36.	Potassium nitrate is called:			(c) hydrolysis of both Na <sup>+</sup> and CO <sub>3</sub> <sup>-</sup> ions
	(a) Mohr's salt $\square$ (b) Indian saltpetre			(d) none of the above
	(c) Gypsum		49.	When chlorine is passed through concentrated solution o
37.	In the following reaction,			KOH, the compound formed is:
	$NaOH + S \longrightarrow A + Na_2S_5 + H_2O$ ,			(a) KClO
	A is:			(c) $KClO_3$
	(a) $Na_2SO_3$ $\square$ (b) $Na_2SO_4$		50.	If NaOH is added to an aqueous solution of Zn <sup>2+</sup> ions,
	(c) $Na_2S_2O_3$ $\square$ (d) $Na_2S$			white precipitate appears and on adding excess of NaOH

	the precipitate dissolves. In the solution, zinc exists in the:	62.	A white solid reacts with dil. HCl to give colourless gas to decolourises aqueous bromine. The solid is most likely	
	(a) anionic part		be:	Ю
	(b) cationic part		(a) sodium carbonate	
	(c) both in anionic and cationic parts		• •	
	(d) colloidal form	63	In the following sequence of reactions, identify	
51.	Which of the following has lowest thermal stability?	05.	compounds $(A)$ , $(B)$ , $(C)$ and $(D)$ :	u.c
J1.	(a) Li <sub>2</sub> CO <sub>3</sub>		SO <sub>2</sub> Na <sub>2</sub> CO <sub>3</sub> S AgNO <sub>3</sub>	
	(c) $K_2CO_3$ $\square$ (d) $Rb_2CO_3$ $\square$	. '	$Na_2CO_3 \xrightarrow{SO_2} (A) \xrightarrow{Na_2CO_3} (B) \xrightarrow{S} (C) \xrightarrow{AgNO_3} (A)$	D)
52.	Which salt on heating does not give brown coloured gas?		Solution (a) No SQ, NoUSQ, No S, A C S	
	(a) LiNO <sub>3</sub>		(a) Na <sub>2</sub> SO <sub>3</sub> , NaHSO <sub>3</sub> , Na <sub>2</sub> S, Ag <sub>2</sub> S	
	(c) $Pb(NO_3)_2$ $\square$ (d) $AgNO_3$ $\square$		(b) NaHSO <sub>3</sub> , Na <sub>2</sub> SO <sub>3</sub> , Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , Ag <sub>2</sub> S (c) NaHSO <sub>3</sub> , Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> S, Ag <sub>2</sub> O	
53.	Fire extinguishers contain H <sub>2</sub> SO <sub>4</sub> and:			
	(a) NaHCO <sub>3</sub> and Na <sub>2</sub> CO <sub>3</sub> □ (b) NaHCO <sub>3</sub> solution □		(d) Na <sub>2</sub> SO <sub>3</sub> , Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , Ag	ш
	(c) Na <sub>2</sub> CO <sub>3</sub>		[Hint: $Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2$	
54.	Which of the following compound is used in gun powder?		$2\text{NaHSO}_3 + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{CO}_2$	
	(a) $LiNO_3$ $\Box$ (b) $NaNO_3$ $\Box$		(B)	
	(c) $Pb(NO_3)_2$ $\square$ (d) $KNO_3$ $\square$		$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$	
55.	Which of the following compounds is(are) not soluble in		(C)	
	water?		$Na_2S_2O_3 + 2AgNO_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$	
	(a) $\text{Li}_2\text{CO}_3$ $\square$ (b) $\text{Li}_7$		$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$	
	(c) Li <sub>3</sub> PO <sub>4</sub>		(D)	
56.	When a standard solution of NaOH is left in air for a few	64	$ZnCl_2 + NaHCO_3 \xrightarrow{\text{Heat}} (A) \xrightarrow{\text{Heat}} (B) + (C) \uparrow + H_2$	n .
	hours:	04.		
	(a) a precipitate will form		$(B) + \text{NaOH} \longrightarrow D$	
	(b) strength will decrease □		Identify the compound $D$ present in the solution :	
	(c) strength will increase		(a) $ZnCO_3$ $\Box$ (b) $Zn(OH)_2$	
	(d) the concentration of $Na^+$ ions will remain constant $\square$		(c) ZnO $\square$ (d) Na <sub>2</sub> ZnO <sub>2</sub>	
57.	The pair of compounds which cannot exist together in		[Hint: $ZnCl_2 + 2NaHCO_3 \longrightarrow Zn(HCO_3)_2 + 2NaCl$	
	solution is:		$Zn(HCO_3)_2 \longrightarrow ZnCO_3 + H_2O + CO_2$ (B) (C)	
	(a) NaHCO <sub>3</sub> and NaOH $\Box$ (b) Na <sub>2</sub> CO <sub>3</sub> and NaHCO <sub>3</sub> $\Box$		$(B) \qquad \qquad (C)$	
	(c) $Na_2CO_3$ and $NaOH$ $\square$ (d) $NaHCO_3$ and $NaCl$ $\square$		$ZnCO_3 + 2NaOH \longrightarrow Zn(OH)_2 + Na_2CO_3$	
58.	Which of the following reaction/s is/are correct?			
	(i) $Cl_2 + NaOH \longrightarrow NaCl + NaClO_2 + H_2O$		$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$ ]	
	(i) $Cl_2 + NaOH \longrightarrow NaCl + NaClO_3 + H_2O$ Conc. and hot	65.	LiAlH <sub>4</sub> is used as:	
	solution (ii) $P_4 + NaOH + H_2O \longrightarrow NaH_2PO_2 + PH_3$		(a) an oxidising agent	
	(ii) $P_4 + NaOH + H_2O \longrightarrow NaH_2PO_2 + PH_3$ (yellow)		(c) a mordant	
	(iii) $S + NaOH \xrightarrow{\text{Heat}} Na_2S_2O_3 + Na_2S + H_2O$	66.	Sodium sulphate is soluble in water whereas barium sulph	ate
	(m) 5 + NaO11		is sparingly soluble because:	
	(iv) $C + NaOH \xrightarrow{Heat} Na_2SiO_3 + H_2$		(a) the hydration energy of sodium sulphate is more that	han
	(a) (i) and (ii) $\square$ (b) (ii) and (iii) $\square$		its lattice energy	
	(c) (i), (ii) and (iii) $\Box$ (d) all are correct $\Box$		(b) the lattice energy of barium sulphate is less than	its
59.	The most abundant alkali metal in nature is:		hydration energy	
٥).	(a) lithium		(c) the lattice energy has no role to play is solubility	
	(c) potassium		(d) the hydration energy of sodium sulphate is less than	its
60.	When sodium hydroxide solution is electrolysed:		lattice energy	U ·
	(a) hydrogen is discharged at cathode □	67.	e e	mic
	(b) hydrogen is discharged at anode □	İ	number of alkali metals increases?	_
	(c) sodium is liberated at anode		(a) Electronegativity	닏
	(d) no hydrogen is liberated		(b) First ionisation potential	닏
61.	In the Castner process for the extraction of sodium, the anode		(c) Ionic radius	니
	is made of : [E.A.M.C.E.T. 2003]	60	(d) Melting point	
	(a) nickel	68.	, L	_
	(c) copper		(a) less electronegativity	
			(b) more ionisation potential	ш

	(c) larger atomic radius		83.	Thermal stability of hydrides of first group elements follows
	(d) lower melting point			the order: [C.B.S.E. 2008]
69.	Which of the following alkali metals does not form alun	ns?		(a) LiH > NaH > KH $\rightarrow$ RbH
	(a) Rb			(b) LiH > KH > NaH > RbH
	(c) Na			(c) LiH > RbH > KH > NaH
70.	Incorrect match is:	_		(d) LiH > KH > RbH > NaH
70.			84.	There occurs loss of mass when a mixture of Li <sub>2</sub> CO <sub>3</sub> and
	(a) Soda ash: $Na_2CO_3$			Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O is heated strongly. The loss of mass is due
	(c) Pearl ash: $K_2CO_3$ $\square$ (d) Baking soda: NaHCC	-		to:
71.	The metallic lustre exhibited by sodium is explained by:			(a) decomposition of Li <sub>2</sub> CO <sub>3</sub> only
	(a) diffusion of sodium ions			(b) loss of water by Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O
	(b) oscillation of mobile valence electrons			(c) both (a) and (b)
	(c) existence of free protons			(d) none of these
	(d) existence of body centred cubic lattice		95	In certain matters, lithium differs from other alkali metals, the
72.	Crude common salt is hygroscopic because of impurities	of:	65.	main reason for this is:
	(a) CaSO <sub>4</sub> and MgSO <sub>4</sub>			(a) small size of lithium atom and Li <sup>+</sup>
	(b) CaCl <sub>2</sub> and MgCl <sub>2</sub>			
	(c) CaBr <sub>2</sub> and MgBr <sub>2</sub>	<u> </u>		(b) extremely high electropositivity of Li
	(d) Ca(HCO <sub>3</sub> ) <sub>2</sub> and Mg(HCO <sub>3</sub> ) <sub>2</sub>	ā		(c) greater hardness of Li (d) hydration of Li <sup>+</sup> ion
73.	Which of the following compounds of potassium is known			(-))
13.	as 'pearl ash'?	JWII	86.	Identify the correct statement. Elemental sodium:
	-			(a) can be prepared and isolated by electrolysing an aqueous
	(a) $K_2CO_3$			solution of sodium chloride
	(c) KCl $\Box$ (d) KNO <sub>3</sub>			(b) is a strong oxidising agent
74.	•	e of		(c) is insoluble in ammonia
	NaOH, the ion discharged at cathode is:			(d) is easily oxidised $\Box$
	(a) $Na^+$		87.	
	(c) $H^+$			(a) Na
75.	When sodium is added in scanty water, it catches fire	. In		(c) K $\square$ (d) Rb $\square$
	this process which one of the following burns?		88.	Which of the following compounds on reaction with NaOH
	(a) Na $\Box$ (b) H <sub>2</sub> O			and H <sub>2</sub> O <sub>2</sub> gives yellow colour?
	(c) CO $\Box$ (d) $H_2$			(a) $Zn(OH)_2$ $\Box$ (b) $Cr(OH)_3$ $\Box$
76.	Among LiCl, RbCl, BeCl <sub>2</sub> and MgCl <sub>2</sub> the compounds	with	İ	(c) $Al(OH)_3$ $\Box$ (d) None of these $\Box$
	greatest and least ionic character respectively are:		89.	The stability of the following alkali metal chlorides follows
	(a) LiCl, RbCl			the order:
	(c) RbCl, MgCl <sub>2</sub> $\square$ (d) MgCl <sub>2</sub> , BeCl <sub>2</sub>			(a) LiCl > KCl > NaCl > CsCl
<i>7</i> 7.	Stable oxide is obtained by heating the carbonate of	_		(b) CsCl > KCl > NaCl > LiCl
,,,	element:	uic		(c) NaCl > KCl > LiCl > CsCl
	(a) Li			(d) KC1 > CsCl > NaCl > LiCl
	(c) K		90.	Which of the following has the highest melting point?
78.	The chloride that can be extracted with ether is:	<b></b>		(a) NaCl
70.				(c) NaBr
	(a) NaCl (b) KCl		91	Oxone is: [P.M.T. (Manipal) 2001]
70	(c) LiCl	<u></u>	71.	(a) CaO $\square$ (b) N <sub>2</sub> O $\square$
79.	Prefix 'alkali' for alkali metals denotes:	_	j	(c) $Na_2O_2$ $\square$ (d) $NaBO_3$ $\square$
	(a) silvery lustre		m	
	(c) active metals		92.	
80.	2 7			[P.M.T. (M.P.) 2002]
	(a) due to small size of lithium			(a) weak oxidising agents
	(b) due to high hydrogen number of lithium			(b) strong reducing agents
	(c) due to high ionisation energy of lithium			(c) strong oxidising agents $\square$
	(d) none of the above			(d) weak reducing agents $\square$
81.	For the preparation of sodium thiosulphate by "Spri	ng's	93.	Which of the following has lowest melting point?
	reaction", the reactants used are: [E.A.M.C.E.T.2	003]		[B.V. (Pune) 2002]
	(a) $Na_2S + Na_2SO_3 + Cl_2 \square$ (b) $Na_2S + SO_2$			(a) Li
	(c) $Na_2S + Na_2SO_3 + I_2$			(c) K
82.			94,	When sodium is treated with sufficient oxygen/air, the
	(a) decreases		77.	product obtained is: [A.F.M.C. 2002]
	(c) remains the same  (d) none of these	П	1	product obtained is. [A.F.W.C. 2002]

	1																		
_ /	tusu	rec		1 12				- :			-			,					
1.	(d)	2.	(c)	3.	(a)	4.	(a)	5.	(b)	6.	(b)	7.	(c)	8.	(c)	9.	(d)	10.	(c)
11.	(a)	12.	(d)	13.	(d)	14.	(a)	15.	(b)	16.	(c)	17.	(b)	18.	(d)	19.	(a)	20.	(c)
21.	(d)	22.	(a)	23.	(b)	. 24.	(c)	25.	(b)	26.	(c)	27.	(a)	28.	(c)	29.	(b)	30.	(d)
31.	(b)	32.	(a)	33.	(a)	34.	(a)	35.	(d).	36.	(b)	37.	(c)	38.	(a)	39.	(c)	40.	(b)
41.	(c)	42.	(a)	43.	· (d)	44.	(b)	45.	(c)	46.	(b)	47.	(a)	48.	(b)	49.	(c)	50.	(a)
51.	(a)	52.	(b)	53.	(a)	54.	(d)	55,	(d)	56.	(b)	57.	(d)	58.	(c)	59.	(b)	60.	(a)
61.	(a)	62.	(d)	63.	(b)	64.	(d)	65.	(b) ·	66.	(a)	67.	(c)	68.	(b)	69.	(d)	70.	(b)
71.	(b)	72.	(b)	73.	(a)	74.	(c)	75.	(d)	76.	(b)	77.	(a)	78.	(c)	79.	(d)	80.	(a)
81.	(c) .	82.	(a)	83.	(a)	84.	(c)	85.	(a)	86.	(d)	87.	(b)	88.	(b)	89,	(d)	90.	(b)
91.	(c)	92.	(b)	93.	(d)	94.	(b)	95.	(a)	96.	(d)	97.	(a)	98.	(b)	99.	(d)	100.	(a)
101.	(a)	102.	(d)	103.	(a)	104.	(a)	105.	(b)	106.	(d)	107.	(a)	108.	(b)	109.	(a)	110.	(d)
111.	(d)	112.	(d)	113.	(b)	114.	(c) ·	115.	(c)	116.	(c)	117.	(a)	118.	(d)	119.	(b)	120.	(d)
121.	(c, d)	122.	(a,b)	123.	(a,b,d)	124.	(a,b,c)	125.	(b,d)	126.	(a,d)	127.	(a, d)	128.	(c, d)	129.	(a,b,c)	130.	(b,c,d)
131.	(a,b,d)	132.	(a h c)	133.	(b)	134	(a.b)												

## **Objective Questions for IIT ASPIRANTS**



- Zinc on reaction with NaOH gives a salt (A) along with a gas (X) and (A) on reaction with a gas (Y) gives white precipitate (W). Which of the following is correct?
  - (a) (A) is  $Na_4ZnO_3$ , (Y) is  $H_2S$  (b) (X) is  $H_2$ , (W) is Zn (OH)<sub>2</sub> (c) (A) is  $Na_2ZnO_2$ , (X) is  $O_2$  (d) (W) is ZnS, (X) is  $H_2$

$$[\textbf{Hint}: Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2 \ ;$$

$$Na_2ZnO_2 + H_2S \longrightarrow ZnS + 2NaOH]$$

$$(Y) \qquad (W)$$

- 2. For Na + NH<sub>3</sub>  $\longrightarrow$  (A)  $\xrightarrow{\text{N}_2\text{O}}$  (B)  $\xrightarrow{\text{Heat}}$  gas (X),
  - Which of the following is correct?
  - (a) (A) on reaction with water gives NaOH and N<sub>2</sub>
  - (b) (B) contains anion of linear geometry
  - (c) (X) is coloured
- (d) All are correct

(c) (X) is coloured (d) All are correct

[Hint: Na + NH<sub>3</sub> 
$$\longrightarrow$$
 NaNH<sub>2</sub>  $\xrightarrow{N_2O}$  NaN<sub>3</sub>  $\longrightarrow$  Na + N<sub>2</sub>
(A) (B) (X)

The anion in (B) is  $N_3^-$  which possesses a linear geometry.

- CO<sub>2</sub> gas along with solid (Y) is obtained when sodium salt (X) is heated. (X) is again obtained when  $CO_2$  gas is passed into aqueous solution of (Y). (X) and (Y) are:
  - (a) Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>O
- (b) Na<sub>2</sub>CO<sub>3</sub>, NaOH
- (c) NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>
- (d) Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>

[Hint: 
$$2NaHCO_3 \xrightarrow{Heat} Na_2CO_3 + H_2O + CO_2$$
;  
 $(X)$   $(Y)$   
 $Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$ ]  
 $(X)$   $(Y)$ 

- For Na + PH<sub>3</sub>  $\longrightarrow$  (A) + gas(X), Na + NH<sub>3</sub>  $\longrightarrow$  (B) + gas
  - (X), which of the following is correct?
  - (a) The anion of (A) is trinegative while the anion of (B) on reaction with acetylene gives ammonia
  - (b) The anion of both (A) and (B) are uninegative
  - (c) The anion of both (A) and (B) are trinegative
  - (d) None of the above

[Hint: 
$$3\text{Na} + \text{PH}_3 \longrightarrow \text{Na}_3\text{P} + \frac{3}{2}\text{H}_2$$
;  
 $Na + \text{NH}_3 \longrightarrow \text{Na}_2\text{NH}_2 + \frac{1}{2}\text{H}_2$ ;  
 $(B)$ 

$$NaNH_2 + C_2H_2 \longrightarrow NaC_2H + NH_3$$

- 5. Sodium oxide can be obtained by heating:
  - (a) sodium carbonate alone
- (b) sodium nitrate alone
- (c) sodium nitrite with sodium (d) none of these
- [Hint:  $2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$ ]
- **6.**  $A + \text{Na}_2\text{CO}_3 \longrightarrow B + C$

 $CO_2$  Milky cloud, C

The chemical formulae of A, B and C are:

$$A \qquad B \qquad C$$

- (a)  $Ca(OH)_2$ CaCO<sub>3</sub> NaOH
- Ca(OH)<sub>2</sub> CaCO<sub>3</sub> (b) NaOH
- (c) NaOH CaO CaCO<sub>3</sub>
- (d) CaO Ca(OH)2 NaOH

[Hint: 
$$Ca(OH)_2 + Na_2CO_3 \longrightarrow 2NaOH + CaCO_3$$

$$(B) \qquad (CO_2) \longrightarrow CaCO_3$$

- 7. An aqueous solution of an halogen salt of potassium reacts with same halogen X to give  $KX_3$ , a violet coloured solution which is used in volumetric exercises (iodimetric titrations). The halogen X is:
  - (a) fluorine
- (b) bromine
- (c) chlorine
- (d) iodine

[**Hint**:  $KI + I_2 \longrightarrow KI_3$  (violet coloured solution)]

- **8.** In LiAlH<sub>4</sub>, metal Al is present in:
  - (a) cationic part
  - (b) anionic part
  - (c) in both cationic and anionic parts
  - (d) neither in cationic nor in anionic part

[Hint: LiAlH<sub>4</sub> 
$$\rightleftharpoons$$
 Li<sup>+</sup> + AlH<sub>4</sub> | Anion

- 9. When sodium reacts with excess of oxygen, oxidation number of oxygen changes from:
  - (a) 0 to -1
- (b) 0 to -2
- (c) -1 to -2
- (d) + 1 to -1

- 10. Sodium is heated in air at 350°C to form X. X absorbs CO<sub>2</sub> and forms sodium carbonate and Y. Which of the following is Y?
  - (a) H<sub>2</sub>

(c)  $H_2O_2$ 

(d)  $O_3$ 

[Hint: 2Na  $\frac{O_2}{\text{(air)}}$  Na<sub>2</sub>O<sub>2</sub>; 2Na<sub>2</sub>O<sub>2</sub> + 2CO<sub>2</sub>  $\rightarrow$  2Na<sub>2</sub>CO<sub>3</sub> + O<sub>2</sub>]

- 11. Which disproportionates on heating with NaOH?
  - (a)  $P_4$

(c) Cl<sub>2</sub>

(d) All of these

[Hint: 
$$P_4$$
 + 3NaOH + 3H<sub>2</sub>O  $\longrightarrow$  3NaH<sub>2</sub>PO<sub>2</sub> + PH<sub>3</sub>

$$4S + 6NaOH \longrightarrow Na_2S + Na_2S_2O_3 + 3H_2O$$

$$(-2) \qquad (+2)$$

$$3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

- 12. On heating a mixture containing 1 mole each of Li<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>.....is/are formed.
  - (a) 2 moles of CO<sub>2</sub>
- (b) 1 mole of CO<sub>2</sub>
- (c) 1.5 moles of CO<sub>2</sub>
- (d) no carbon dioxide

[Hint: Li<sub>2</sub>CO<sub>3</sub> decomposes while K<sub>2</sub>CO<sub>3</sub> is stable and does not decompose.

$$\begin{array}{ccc} \text{Li}_2\text{CO}_3 & \longrightarrow \text{Li}_2\text{O} & + \text{CO}_2 \text{ ]} \\ \text{I mole} & \text{I mole} \end{array}$$

13. When a substance A reacts with water it produces a combustible gas B and a solution of a substance C in water. When another substance D reacts with this solution of C, it also produces the same gas B on warming, but D can produce B on reaction with dilute sulphuric acid at room temperature. A imparts a deep golden yellow colour to a smokeless flame of Bunsen burner. A, B, C and D respectively are:

- (a) Na, H2, NaOH and Zn
- (b) K, H<sub>2</sub>, KOH and Al
- (c) Ca, H<sub>2</sub>, Ca (OH)<sub>2</sub> and Sn
- (d) CaC2, C2H2, Ca (OH)2 and Sn

[Hint: Na + H<sub>2</sub>O 
$$\longrightarrow$$
 NaOH + H<sub>2</sub>;  
(A) (C) (B)  
 $+Zn$   
(D)
$$Zn + H2SO4  $\longrightarrow$  ZnSO<sub>4</sub> + H<sub>2</sub>]$$

14. What is the heat of solution of sodium chloride from following data?

Hydration energy of Na<sup>+</sup> = -389.4 kJ mol<sup>-1</sup> Hydration energy of Cl<sup>-</sup> = -382.3 kJ mol<sup>-1</sup> Lattice energy of NaCl = -776 kJ mol<sup>-1</sup>

(a)  $+ 8.6 \text{ kJ mol}^{-1}$ 

(b) +  $4.3 \text{ kJ mol}^{-1}$ 

(c)  $-4.3 \text{ kJ mol}^{-1}$ 

(d)  $- 8.6 \, \text{kJ mol}^{-1}$ 

[Hint:  $\Delta H_{\text{sol.}}$  = Hydration energy - Lattice energy Hydration energy of NaCl = -389.4-382.3 = -771.7 kJ mol<sup>-1</sup>]

- **15.** There is loss in mass when mixture of Li<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O is heated strongly. The loss is due to:
  - (a) Li<sub>2</sub>CO<sub>3</sub> only
  - (b) Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O only
  - (c) both Li<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O
  - (d) none of the above
- 16. A colourless solid (X) on heating evolved CO<sub>2</sub> and also gave a white residue, soluble in water. Residue also gave CO<sub>2</sub> when treated with dilute acid (X) is:
  - (a) Na<sub>2</sub>CO<sub>3</sub>

(b) CaCO<sub>3</sub>

(c) NaHCO<sub>3</sub>

(d) Ca(HCO<sub>3</sub>)<sub>2</sub>

White ppt.

[Hint: 
$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$
]

Acid

Soluble  $CO_2$ 

in water

17. CO + NaOH 
$$\xrightarrow{200^{\circ}\text{C}}$$
 (A)  $\xrightarrow{\text{Heat}}$  (B)  $\downarrow$  CaC

(A) and (B) are:

(a) NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>

(b) HCOONa, COONa

COONa

(c) HCOONa, NaOH

(d) NaHCO<sub>3</sub>, NaOH

$$\begin{array}{c}
COONa \\
COONa \\
COONa
\end{array} + CaCl_2 \longrightarrow \begin{array}{c}
COO \\
| \\
COO \\
White ppt.
\end{array}$$

- 18. Select the correct statement:
  - (a) Solubility of alkali hydroxides is in order: CsOH > RbOH > KOH > NaOH > LiOH
  - (b) Solubility of alkali carbonates is in order : Li<sub>2</sub>CO<sub>3</sub> > Na<sub>2</sub>CO<sub>3</sub> > K<sub>2</sub>CO<sub>3</sub> > Rb<sub>2</sub>CO<sub>3</sub> > Cs<sub>2</sub>CO<sub>3</sub>
  - (c) both are correct
  - (d) none of the above is correct
- 19.  $NH_4Cl + (A) \longrightarrow Microcosmic salt$

$$(B) \xrightarrow{\text{Heat} \atop +\text{MnO}} (C)$$
Violet bead

- (A), (B) and (C) are:
- (a) Na<sub>3</sub>PO<sub>4</sub>, NaPO<sub>3</sub>, (Mn)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>
- (b) Na<sub>2</sub>HPO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>
- (c) Na<sub>2</sub>HPO<sub>4</sub>, NaPO<sub>3</sub>, Mn(PO<sub>3</sub>)<sub>2</sub>
- (d) Na<sub>2</sub>HPO<sub>4</sub>, NaPO<sub>3</sub>, NaMnPO<sub>4</sub>

[Hint: NH<sub>4</sub>Cl + Na<sub>2</sub>HPO<sub>4</sub>  $\longrightarrow$  NaNH<sub>4</sub>HPO<sub>4</sub>
(A) Microcosmic salt

$$IaPO_3 \xrightarrow{Heat} MnNaPO_4$$
Violet bead

- **20.** The aqueous solution of an unknown sodium salt gives the following reactions:
  - (I) It gives white turbidity with dilute HCl solution.
  - (II) It decolourises a solution of iodine in potassium iodide.
  - (III) It gives a white precipitate with AgNO<sub>3</sub> solution which changes colours and finally becomes black on standing.

The unknown sodium salt is:

- (a) sodium sulphite
- (b) sodium sulphide
- (c) sodium bisulphite
- (d) sodium thiosulphate

 $[\textbf{Hint:} (i) \quad Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + H_2O + S$ 

(ii)  $KI_3 + 2Na_2S_2O_3 \longrightarrow KI + 2NaI + Na_2S_4O_6$ 

(iii)  $2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$ White

 $\begin{array}{c}
H_2O \\
\longrightarrow Ag_2S + H_2SO_4
\end{array}$ Black

#### 3. (c) 1. (d) 2. (b) 4. (a) 6. (a) 7. (d) **8.** (b) 12. (b) **5.** (c) **9.** (a) **10.** (b) **11.** (d) 13. (a) 15. (c) 17. (b) 19. (d) 20. (d) 14. (b) **16.** (c) 18. (a)

# Matrix Matching Questions for IIT Aspirants

1	Matah	Tiot I	*****	List-II:
1.	IVIAICH	LiSt-1	with	LASU-II.

#### List-I

#### List-II

- (a) Triphylite
- (p) Ore of lithium
- (b) Amblygonite
- (q) Phosphate ore
- (c) Natron
- (r) Borax
- (d) Tincal
- (s) Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O
- Match the compounds in List-I with their colour in List-II:

#### List-I

#### List-II

(a) Li<sub>3</sub>N

(p) Pale yellow

(b) K<sub>2</sub>O

- (q) Orange
- (c) Cs<sub>2</sub>O (d) Rb<sub>2</sub>O
- (r) Colourless (s) Ruby red
- (e) Li<sub>2</sub>O
- Match the compounds of List-I with their composition of List-II:

#### List-I

#### List-II

- (a) Black ash
- (p)  $K_2CO_3$
- (b) Washing soda
- (q) CaS
- (c) Nitrolim
- (r) Na<sub>2</sub>CO<sub>3</sub>
- (d) Pearl ash
- (s)  $CaCN_2 + C$
- Match List-I with List-II:

## List-I

## List-Ⅱ

- (a) Alkali metal with highest m.pt.
- (p) Water

(e-r)

- (c) Sodium cannot be stored under
- (b) Alkali metal with least metallic character (q) Li (r) Ionic hydride
- (d) CaH<sub>2</sub>

(s) Hydrolith

5. Match List-II with List-II:

#### List-I

### List-II

- (a) Na
- (p) Stored in kerosine
- (b) NaHCO<sub>3</sub>
- (q) Used in photoelectric cell

(s) Component of baking powder

- (c) K
- (d) Cs

- (r) Stored in benzene
- Match List-I with List-II:

## List-I

#### List-II

- (a) Efflorescent
- (b) Deliquescent
- (p) NaOH (q) KOH
- (c) Fusion mixture
- (r) Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>
- (d) Washing soda
- (s) Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O
- 7. Match List-I with List-II:

## List-I

## List-II

- (a) Refractory metal
- (p) Li (q) Mg
- (b) Metal used in the Grignard reagent (c) The metal which form
- (r) Cs
- hydrated chloride
- (d) Metal used in the photoelectric cell
  - (s) K
- Match List-I with List-II:

## List-I

- List-II (Oxide)
- (Alkali metal) (a) Na
- (p) Superoxide
- (b) Cs

(q) Coloured oxide

(c) K

(r) Stable peroxide

(d) Li-

(s) Normal oxide

## aswers

(a-p, q) (a-s)

(a-q, r)

(a-q)

(b-p, q) (b-p)

(b-r)

(b-q)

(c-s)(c-q)

(c-s)

(c-p)

- (d-r)
- (d-p)
- (d-p)
- (d-r, s)

(a-p, r)

(a-q)

- (b-s)
- (c-p, q, r)
- (d-p, q, r)

- (a-s).
- (b-p, q)(b-q)
- (c-r)
- (d-s)(d-r, s)

(a-r)

7.

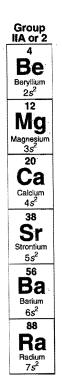
- (b-p, q)
- (c-p, q) (c-p, q)
- (d-s)

# Assertion-Reason Type Questions

The following questions consist of an Assertion (A) and Reason (R). Use the following key to choose the appropriate

- answer. (a) If both (A) and (R) are correct and (R) is the correct
  - explanation of (A). (b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
  - If (A) is correct but (R) is not correct.
  - (d) If both (A) and (R) are not correct.
- 1. (A) Lithium resembles magnesium, diagonally placed in IIA
  - (R) The sizes of lithium and magnesium atoms and their ions (Li<sup>+</sup> and Mg<sup>2+</sup>) are nearly the same. [A.I.I.M.S. 1997]

- 2. (A) Lithium chloride is predominantly covalent compound.
  - (R) Electronegativity difference between Li and Cl is small.
    - [LLT. 1998]
- 3. (A) Alkali metals do not occur in native state.
  - (R) Alkali metals are highly reactive metals.
- **4.** (A) K<sub>2</sub>CO<sub>3</sub> cannot be prepared by Solvay process.
  - (R) K<sub>2</sub>CO<sub>3</sub> does not decompose on heating.
- 5. (A) Sodium metal when dissolved in liquid ammonia forms a blue coloured solution.
  - (R) The blue solution is a good conductor of electricity.
- 6. (A) Among the alkali metals, caesium salts exhibit the maximum electrical conductance in aqueous solutions.
  - (R) Bigger the radius of the hydrated cation, higher is the electrical conductance of the aqueous solution.



# CHAPTER



# Alkaline Earth Metals and their Compounds

(Group IIA or 2,  $ns^2$ )

## Contents:

- 7.1 Position of Alkaline Earth Metals in Periodic Table
- **7.2** Solubility of Compounds of Alkaline Earth Metals
- 7.3 Difference between Alkaline Earth Metals and Alkali Metals
- 7.4 Abnormal Behaviour of Beryllium
- 7.5 Similarities (Diagonal Relationship) between Beryllium and Aluminium
- 7.6 Magnesium
- 7.7 Calcium
- 7.8 Compounds of Barium

Group	IA	HA	ША
Period	1	2	13
2	Li	Be	B
	(3)	(4)	(5)
3	Na	Mg	Al
	(11)	(12)	(13)
4	K	Ca	Ga
	(19)	(20)	(31)
5	Rb	Sr	In
	(37)	(38)	(49)
6	Cs	Ba	T1
	(55)	(56)	(81)
7	Fr	Ra	Uut
	(87)	(88)	(113)

# POSITION OF ALKALINE EARTH METALS IN PERIODIC TABLE

The group IIA of the periodic table consists of six elements—beryllium, magnesium, calcium, strontium, barium and radium. These elements are collectively called as **alkaline earth metals** because their earths (the old name for oxide) are basic (alkaline) and group IIA is known as **alkaline earth group**. The oxides of three principal members calcium, strontium and barium were known much earlier than the metals themselves. These oxides were alkaline in nature and existed in the earth and were named **alkaline earths**. The metals when discovered were also called alkaline earths. This term is now applied to all the six elements of group IIA. The first member beryllium is less active than other members and shows some abnormal properties like lithium in IA group. However, it shows resemblance with aluminium (a member of IIIrd group), *i.e.*, diagonal relationship. The last member, radium\* is radioactive in nature. Each member of this group occupies a place just after the members of IA group in various periods of periodic table except first period.

IA	Li 3	Na 11	K 19	Rb 37	Cs 55	Fr 87
ΠA	Be 4	Mg 12	Ca 20	Sr 38	Ba 56	Ra 88

The members of this group show a marked resemblance in their properties and possess same electronic configuration. There is gradual gradation in the properties with the increase of atomic number. This justifies their inclusion in the same group of periodic table. The main properties are discussed below for this justification.

## 1. Electronic Configuration

The valence electron configuration of the atoms of the group IIA elements is  $ns^2$ , where n is the period number. The arrangement or the distribution of

<sup>\*</sup>Radium and its all isotopes are radioactive. The longest lived isotope being Ra<sup>226</sup> with half-life 1600 years. This isotope is formed in natural decay series of U<sup>238</sup>.

electrons on	various	subshells	in	the	atoms	of	alkaline	earth	metals:	s give	n below:	
--------------	---------	-----------	----	-----	-------	----	----------	-------	---------	--------	----------	--

Element	At. No.		Electronic Configuration	Configuration of the valency shell
Be	4	2, 2	$1s^2$ , $2s^2$	[He] 2s <sup>2</sup>
Mg	12	2, 8, 2	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$	[Ne] 3s <sup>2</sup>
Ca	20	2, 8, 8, 2	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ , $4s^2$	[Ar] $4s^2$
Sr	38	2, 8, 18, 8, 2	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ , $5s^2$	[Kr] $5s^2$
Ba	56	2, 8, 18, 18, 8, 2	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ , $5s^2$ $5p^6$ , $6s^2$	[Xe] $6s^2$
Ra	88	2, 8, 18, 32, 18, 8, 2	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ , $5s^2$ $5p^6$ $5d^{10}$ , $6s^2$ $6p^6$ , $7s^2$	[Rn] 7s <sup>2</sup>

The outermost shell of these elements has two electrons and the penultimate shell contains 8 electrons except the first member which contains 2 electrons. Since, the last electron enters ns orbital, these are s-block elements. Beryllium shows somewhat abnormal properties as its electronic configuration is slightly different than the rest of the members. Because of their similarity in electronic configuration [noble gas]  $ns^2$ , they are included in the same group, *i.e.*, IIA of the periodic table and closely resemble each other in the physical and chemical properties.

## 3 2. Physical Properties

(a) **Physical state:** All the group IIA elements are metals and too reactive, so that cannot occur in the uncombined state in nature. They are all silvery white metals. They have greyish white lustre when freshly cut, but tarnish soon after their exposure in air due to surface oxidation (Fig. 7.1). They are

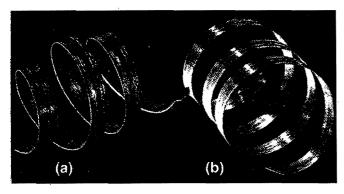


Fig. 7.1 Tarnished (a) and cleaned-up (b) magnesium

soft in nature but harder than alkali metals because metallic bonding is stronger than IA elements due to possession of 2 valency electrons. However, hardness decreases with increase in atomic number.

(b) Atomic and ionic radii: The size of the atom increases gradually from Be to Ra, on account of the presence of an extra energy shell at each step. The atoms are large but smaller than corresponding IA elements since the extra charge on the nucleus attracts the electron cloud inwards. Their ions are also large and size of the ion increases from Be<sup>2+</sup> to Ra<sup>2+</sup>.

•	Be	Mg	Ca	Sr	Ba	Ra
Atomic radii (pm)	112	160	197	215	222	
(Metallic radii) Ionic radii (pm) (M <sup>2</sup>	<sup>t</sup> ) 31	72	100	118	135	148

Atomic volume also increases as the atomic number increases.

(c) **Density:** These metals are denser than alkali metals in the same period because these can be packed more tightly due to their **greater nuclear charge and smaller size.** The density decreases slightly upto calcium and then increases considerably upto radium. Irregular trend is due to the difference in the crystal structure of these elements.

(d) Melting and boiling points: The melting and boiling points of these elements are higher than corresponding alkali metals. This is due to the presence of two electrons in the valency shell and thus, strongly bonded in the solid state. However, melting and boiling points do not show any regular trend because atoms adopt different crystal structures.

	Be	Mg	Ca	Sr	Ba	Ra
m.pt. (K)	1560	924	1124	1062	1002	973
b.pt. (K)	2745	1363	1767	1655	2078	

(e) Ionisation energies and electropositive character: The first and second ionisation energies of these metals decrease from Be to Ba. The second ionisation energy in each case is higher than the first, nearly double the first ionisation energy.

The ionisation energy of last member, radium, is slightly higher than that of barium and it is difficult to explain this anomalous behaviour.

Although, the ionisation energies of these elements are higher than those of alkali metals, yet these are sufficiently low to make these atoms to lose two electrons of their valency shell to form  $M^{2+}$  ions and achieve the inert gas configuration. These

## 7.3 DIFFERENCE BETWEEN ALKALINE EARTH METALS AND ALKALI METALS

Both alkaline earth metals and alkali metals are s-block elements as the last differentiating electron enters the ns-orbital. They resemble with each other in many respects but still there are certain dissimilarities in their properties on account of different number of electrons in the valency shell, smaller atomic radii, high ionisation potential, higher electronegativity, etc. The main points of difference between alkaline earth metals and alkali metals are given below:

	Properties	Alkaline earth metals	Alkali metals
(i)	Electronic configuration	Two electrons are present in the valency shell. The configurations is $ns^2$ .	One electron is present in the valency shell. The configuration is $ns^1$ .
(ii)	Valency	Bivalent.	Monovalent.
(iii)	Electropositive nature	Less electropositive.	More electropositive.
(iv)	Hydroxides	Weak bases, less soluble and decompose on heating.	Strong bases, highly soluble and stable towards heat.
(v)	Bicarbonates	These are not known in free state. Exist only in solution.	These are known in solid state.
(vi)	Carbonates	Insoluble in water. Decompose on heating.	Soluble in water. Do not decompose on heating (Li <sub>2</sub> CO <sub>3</sub> is an exception).
(vii)	Action of nitrogen	Directly combine with nitrogen and form nitrides.	Do not directly combine with nitrogen.
(viii)	Action of carbon	Directly combine with carbon and form carbides.	Do not directly combine with carbon.
(ix)	Nitrates	Decompose on heating evolving a mixture of NO <sub>2</sub> and oxygen.	Decompose on heating evolving only oxygen.
(x)	Solubility of salts	Sulphates, phosphates, fluorides, chromates, oxalates, etc., are insoluble in water.	Sulphates, phosphates, fluorides, chromates, oxalates, etc., are soluble in water.
(xi)	Physical properties	Are less reactive and comparatively harder metals. High melting points. Diamagnetic.	Soft, low melting points. Paramagnetic.
(xii)	Hydration of compounds	The compounds are extensively hydrated. MgCl <sub>2</sub> ·6H <sub>2</sub> O,	The compounds are less hydrated. NaCl, KCl and
(xiii)	Reducing power	CaCl <sub>2</sub> ·6H <sub>2</sub> O and BaCl <sub>2</sub> ·2H <sub>2</sub> O are hydrated chlorides. Weaker, as ionisation potential values are high and oxidation potential values are low.	RbCl form non-hydrated chlorides. Stronger, as ionisation potential values are low and oxidation potential values are high.

# 7.4 ABNORMAL BEHAVIOUR OF BERYLLIUM

Beryllium is a much less abundant alkaline earth metal, although masses of the mineral beryl (Be<sub>3</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>) that weigh as much as a ton have been found. Pure beryl is colourless, but impurities give it colour; chromium as an impurity makes beryl into emerald (Fig. 7.2) and iron makes it aquamarine. Beryllium differs from rest of the alkaline earth metals on account of its small atomic size, high electronegativity and slight difference in electronic configuration. Be<sup>2+</sup> is very small. It exerts a high polarising effect on any anion associated with it. On account of this, beryllium compounds show covalent character. Its compounds have low melting points and are soluble in organic solvents. These are hydrolysed in water.

## The main points of difference are given below:

- (i) It is the hardest of all alkaline earth metals: This is due to the fact that maximum metallic bonding is present on account of the smallest size amongst alkaline earth metals.
- (ii) The melting and boiling points of the beryllium are the highest: This is also due to maximum metallic bonding.
- (iii) It is not affected by atmosphere: Be is least reactive as its ionisation potential is high. However, it does react with oxygen and nitrogen at high temperatures.
- (iv) It does not decompose water: This is due to low value of oxidation potential.

- (v) It has the tendency to form covalent compounds: The polarisation effect of Be<sup>2+</sup> ion is high due to its high charge density. The large distortion of electron cloud of the anion brings covalent character. Be has high value of electronegativity (1.5) and when it reacts with another element, the electronegativity difference is not so large and the bond is, therefore, covalent.
- (vi) It does not react directly with hydrogen: Beryllium hydride can, however, be formed by reducing BeCl<sub>2</sub> with LiAlH<sub>4</sub>. Beryllium hydride is a covalent compound. It is polymeric solid,  $(BeH_2)_n$ . It contains hydrogen bridges between beryllium atoms.

The hydrides of Ca, Sr and Ba are largely ionic due to greater electropositive character.

(vii) It dissolves in alkalies with evolution of hydrogen:

Be + 2NaOH + 2H<sub>2</sub>O 
$$\longrightarrow$$
 Na<sub>2</sub>BeO<sub>2</sub>·2H<sub>2</sub>O + H<sub>2</sub>  
Sodium beryllate

other alkaline earth metals do not react with alkalies.

- (viii) It does not liberate hydrogen from acids readily: This is due to the fact that Be has lowest oxidation potential amongst alkaline earth metals.
- (ix) Its oxide is amphoteric in nature: Be is thus weak electropositive in nature.

$$BeO + H2SO4 \longrightarrow BeSO4 + H2O$$

$$BeO + 2NaOH \longrightarrow Na2BeO2 + H2O$$

The oxide is sparingly soluble in water as it has high degree of covalency. It has high melting point (approx. 2500°C). The high melting point of BeO is due to its polymeric nature.

The oxides of other alkaline earth metals are basic, soluble and ionic in nature. The basic nature increases in moving down the group.

BeO has a 4:4 zinc sulphide (Wurtzite) structure, but all others have a 6:6 sodium chloride structure.

(x) Its hydroxide is amphoteric in nature: Be is thus weak electropositive in nature.

$$Be(OH)_2 + 2HCl \longrightarrow BeCl_2 + 2H_2O$$
  
 $Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$ 

The hydroxide is insoluble in water. It is covalent in nature. The hydroxides of other alkaline earth metals are basic, ionic and their solubility increases on moving from Mg(OH)<sub>2</sub> to Ba(OH)<sub>2</sub>.

## (xi) Its carbide (Be<sub>2</sub>C) on hydrolysis evolves methane : $Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$

The carbides of other alkaline earth metals  $(MC_2)$  evolve acetylene on hydrolysis.

(xii) Its carbonate (BeCO<sub>3</sub>) is not stable towards heat:

The instability is due to strong polarising effect of small  $Be^{2+}$  ion on the large  $CO_3^{2-}$  ion.

- (xiii) Its nitride ( $Be_3N_2$ ) is volatile:  $Be_3N_2$  is covalent, while nitrides of other alkaline earth metals are ionic crystalline compounds.
- (xiv) Its sulphate is soluble in water: It is due to high degree of solvation of small  $Be^{2+}$  ions.
- (xv) BeCl<sub>2</sub> is a covalent compound: It does not conduct electricity in fused state. It is soluble in organic solvents and acts as a Lewis acid. It fumes in air.

The chlorides of other alkaline earth metals are ionic and good conductors of electricity in fused state and in solutions.

- (xvi) It is rendered passive by concentrated nitric acid: Nitric acid is an oxidising agent. It forms unreactive thin layer of oxide on its surface and makes the metal passive.
- (xvii) Its compounds do not impart any colour to flame: Very high energy is required to excite electron from lowest energy shell.
- (xviii) Its salts can never have more than four molecules of water of crystallisation as it has only four available orbitals in its valency shell.

Other alkaline earth metals can extend their coordination number to 6 by using d-orbitals.

(xix) It has strong tendency to form complex compounds: Beryllium ion, on account of its small size, forms stable complexes, such as  $[BeF_3]^-$  or  $[BeF_4]^{2-}$ . It forms many chelate like complexes specially with oxygen donors.

- (xx) It has the tendency to form alloys: The metal and its alloys have the following important applications.
  - (a) Low density of beryllium makes it important in the formation of missiles and satellites.
  - (b) Much of the metal that is produced is added in small amounts to copper, the small beryllium atoms pin the copper atoms together in an interstitial alloy that is more rigid than pure copper but still conducts electricity well.
  - (c) The hard electrically conducting alloy is formed for non-sparking tools for use in oil refineries and grain elevators, where there is a risk of explosions.
  - (d) Beryllium is used as windows for X-ray tubes, because beryllium atoms have so few electrons, thin sheets of the metal are transparent to X-rays and allows the rays to escape.

**Note:** The element beryllium occurs mainly as *beryl* 3BeO, Al<sub>2</sub>O<sub>3</sub>.6SiO<sub>2</sub>. Sometime the crystals are so big that they weigh several tonnes. The gemstone *emerald* is a form of *beryl*, its green colour is caused by the Cr<sup>3+</sup> ions present as impurities.

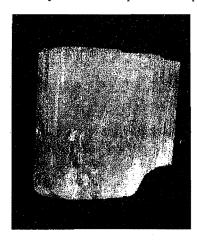


Fig. 7.2 An emerald is a crystal of *beryl* with some Cr<sup>3+</sup> ions which are responsible for the colour



# SIMILARITIES (DIAGONAL RELATIONSHIP) BETWEEN BERYLLIUM AND ALUMINIUM

Beryllium shows some similarities in properties with aluminium, the second typical element of group IIIA (next group in Mendeleev's periodic table) of the next higher period. This type of relationship between diagonally placed elements is called diagonal relationship (one of the characteristics of Mendeleev's periodic table).

$$3MgO + 2Al \longrightarrow 3Mg + Al_2O_3$$
  
 $3MgO + CaC_2 \longrightarrow 3Mg + CaO + 2CO$ 

The reduction is done at 2000°C in vacuum. The vapours of magnesium are condensed.

(ii) Electrolysis of anhydrous magnesium chloride: Carnallite (KCl-MgCl<sub>2</sub>·6H<sub>2</sub>O) is a hydrated compound. It cannot be dehydrated by heating because the water of crystallisation reacts chemically with magnesium chloride to form magnesium oxychloride and finally magnesium oxide.

$$\begin{array}{c} MgCl_2 \cdot 6H_2O \xrightarrow{Heated} MgCl_2 \cdot 2H_2O \xrightarrow{Heated} \\ Hexahydrate & Dihydrate \\ \hline \\ Mg_2OCl_2 \xrightarrow{Strongly} MgO \\ Oxychloride & heated in air \end{array}$$

To make it anhydrous, it is first heated in air and then in a current of HCl gas.

Anhydrous magnesium chloride can also be obtained from MgO or sea water. Chlorine is passed over red hot mixture of MgO and carbon.

$$MgO + C + Cl_2 \longrightarrow MgCl_2 + CO$$

Sea water contains magnesium compounds. It is treated with calcium hydroxide when magnesium hydroxide gets precipitated. It is dissolved in dilute HCl. The solution is then concentrated when hydrated magnesium chloride crystallises out. It is dehydrated as described above.

$$\begin{array}{c} Mg^{2+} + Ca(OH)_2 & \longrightarrow & Mg(OH)_2 + Ca^{2+} \\ (Sea \ water, \ MgCl_2 \ or \ MgSO_4) & ppt. \\ \\ Mg(OH)_2 + 2HCl & \longrightarrow & MgCl_2 \cdot 6H_2O \\ \\ MgCl_2 \cdot 6H_2O & \xrightarrow{Heated} & MgCl_2 + 6H_2O \\ \\ & & Anhydrous \\ \end{array}$$

Finally, the magnesium chloride is dried. The anhydrous magnesium chloride is fused with NaCl and anhydrous calcium

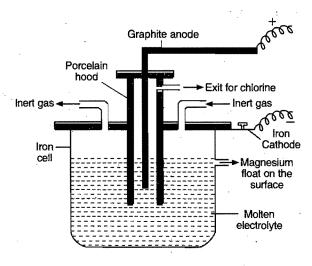


Fig. 7.3 An electrolytic cell

chloride in the ratio of 35% (MgCl<sub>2</sub>); 50% (NaCl) and 15% (CaCl<sub>2</sub>). The mixture is electrolysed at 700°C in presence of an inert gas in an electrolytic cell as shown in Fig. 7.3.

Magnesium is produced at cathode and chlorine at the anode.

$$MgCl_2 \xrightarrow{Electrolysis} Mg + Cl_2$$

Magnesium being lighter than the fused mass floats on the surface from where it is removed periodically by perforated ladles.

The purpose of addition of NaCl and CaCl<sub>2</sub> to anhydrous MgCl<sub>2</sub> is to lower the fusion temperature and make the fused mass good conductor of electricity.

## **Properties**

**Physical Properties:** Magnesium is a silvery-white metal. It is a light metal. It is fairly hard and is malleable and ductile. Its great advantage is its low density (1.74 g/cm<sup>3</sup>), which is only two-thirds that of aluminium 2.70 g/cm<sup>3</sup>. It is sold in the form of ribbons or wire. It melts at 650°C. It is good conductor of heat and electricity.

Chemical Properties: (i) Reaction with air: Pure magnesium metal is a relatively reactive element. It is not affected by dry air. It is slowly tarnished in moist air.

Once magnesium metal has been ignited, it burns vigorously in air to form the oxide with bright white light forming a dense smoke.

$$\begin{array}{ccc} 2Mg \, + \, \mathrm{O}_2 & \longrightarrow & 2Mg\mathrm{O} \\ 3Mg \, + \, N_2(\mathrm{Air}) & \longrightarrow & Mg_3N_2 \end{array}$$

(ii) Reaction with water: Magnesium is not affected by cold water. It decomposes steam or boiling water with evolution of hydrogen.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

(iii) Reaction with acids: It displaces hydrogen from dilute acids.

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$
  
 $Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$   
 $Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$ 

With hot concentrated H<sub>2</sub>SO<sub>4</sub>, it evolves SO<sub>2</sub>.

$$\begin{array}{ccc} H_2SO_4 & \longrightarrow & H_2O + SO_2 + O \\ Mg + O & \longrightarrow & MgO \\ MgO + H_2SO_4 & \longrightarrow & MgSO_4 + H_2O \\ \hline Mg + 2H_2SO_4 & \longrightarrow & MgSO_4 + SO_2 + 2H_2O \\ \end{array}$$

(iv) Reaction with halogens: Magnesium on heating with halogens, readily form halides.

$$Mg + X_2 \longrightarrow MgX_2$$
 $(X \text{ may be F, Cl, Br or I})$ 

(v) Reducing property: Magnesium acts as a strong reducing agent as it has great affinity for oxygen at high temperature. It even burns in the atmosphere of CO<sub>2</sub>, CO, SO<sub>2</sub>, NO, etc.

## The following are the causes of diagonal relationship:

- (a) The polarising power of Be<sup>2+</sup> and Al<sup>3+</sup> ions is high. Consequently the compounds develop covalent nature.
- (b) The standard oxidation potential values of both the elements are very close to each other.
- (c) The electronegativity values of both the elements are the same.

## The similarities in properties are listed below:

- (i) In nature, both the elements occur together in the mineral, beryl, 3BeO·Al<sub>2</sub>O<sub>3</sub>·6SiO<sub>2</sub>.
  - (ii) Both are not affected by atmosphere.
  - (iii) They do not decompose water.
- (iv) Both become passive when treated with concentrated HNO<sub>3</sub>.
  - (v) Both dissolve in caustic alkalies liberating hydrogen.

$$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2$$

$$2AI + 2NaOH + 2H_2O \longrightarrow 2NaAIO_2 + 3H_2$$
Sod. meta

(vi) Both BeO and Al<sub>2</sub>O<sub>3</sub> are amphoteric in nature.

$$BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$$

$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$$

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

Oxides are extremely hard, non-volatile and have high melting points.

(vii) The hydroxides are also amphoteric in nature.

$$Be(OH)_2 + 2HCl \longrightarrow BeCl_2 + 2H_2O$$

$$Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

The hydroxides are insoluble in water and decompose on heating into corresponding oxides.

$$Be(OH)_2 \longrightarrow BeO + H_2O$$

$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

(viii) Beryllium carbide ( $Be_2C$ ) and aluminium carbide ( $Al_4C_3$ ) both evolve methane on treatment with water.

$$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4$$
  
 $Al_4C_3 + 6H_2O \longrightarrow 2Al_2O_3 + 3CH_4$ 

(ix) Both the metals react with halogens and form halides. Chlorides can also be formed in a similar way.

$$BeO + C + Cl_2 \longrightarrow BeCl_2 + CO$$

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$$

The halides (except fluorides) are covalent in nature. They have low melting points and are hydrolysed by water. They dissolve in organic solvents and fume in moist air. The halides behave as Lewis acids.

(x) Beryllium and aluminium both form polymeric covalent hydrides.

(xi) Both combine with nitrogen when strongly heated in its atmosphere.

$$3Be + N_2 \longrightarrow Be_3N_2$$

$$2Al + N_2 \longrightarrow 2AlN$$

Nitrides on action with water evolve ammonia.

$$Be_3N_2 + 6H_2O \longrightarrow 3Be(OH)_2 + 2NH_3$$
  
 $AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$ 

- (xii) Both the metals are obtained by the electrolysis of their fused salts in the presence of fluorides.
- (xiii)  $Be^{2+}$  and  $Al^{3+}$  ions have strong tendency to form chelate type complexes. Both form fluoride complexes, like  $[BeF_4]^{2-}$ ,  $[AlF_6]^{3-}$  respectively.
  - (xiv) The carbonates of both the metals are unstable.
- (xv) Both the ions give hydrated ions in solution (aqueous) like  $[Be(H_2O)_4]^{2+}$  and  $[Al(H_2O)_6]^{3+}$  respectively.
- (xvi) The salts of both Be and Al do not impart a colour to the flame when heated in it.

## 7 MAGNESIUM

**Occurrence:** Magnesium does not occur free in nature. The british chemist Humphry Davy discovered the pure element magnesium in 1808. The name magnesium comes from the name of the mineral **magnesite.** In addition to minerals such as magnesite (MgCO<sub>3</sub>), dolomite (MgCO<sub>3</sub>·CaCO<sub>3</sub>), kieserite (MgSO<sub>4</sub>·H<sub>2</sub>O), epsom salt (MgSO<sub>4</sub>·7H<sub>2</sub>O), carnallite (KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O), asbestos [CaMg<sub>3</sub>(SiO<sub>3</sub>)<sub>4</sub>], it is found in sea water. However magnesium ion, Mg<sup>2+</sup>, is the third most abundant dissolved ion in the oceans, after Cl<sup>-</sup> and Na<sup>+</sup>. The oceans, therefore, are a great source for the supply of the magnesium ion, from which the metal can be obtained easily. It is an essential constituent of chlorophyll, the green colouring matter of plants.

**Extraction:** It is usually extracted by the electrolysis of fused oxide or fused anhydrous magnesium chloride.

(i) From magnesite: The magnesite ore (MgCO<sub>3</sub>) is calcined into magnesium oxide (magnesia).

$$MgCO_3 \xrightarrow{Heated} MgO + CO_2$$

Magnesium may be obtained either by electrolysis or by thermal reduction of magnesium oxide. The oxide is dissolved in a mixture of molten fluorides of magnesium, barium and sodium. The electrolysis of molten mixture is done by using carbon rods as anodes which suspend in molten mass and cast iron rods as cathodes at 650°C. On electrolysis magnesium is obtained in molten state.

The thermal reduction of magnesium oxide can be done by using reducing agents like carbon, silicon, aluminium or calcium carbide.

$$MgO + C \longrightarrow Mg + CO$$
  
 $2MgO + Si \longrightarrow 2Mg + SiO_2$ 

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The thermal reduction of magnesium oxide can be done by using reducing agents like carbon, silicon, aluminium or calcium carbide.

$$MgO + C \longrightarrow Mg + CO$$
  
 $2MgO + Si \longrightarrow 2Mg + SiO_2$ 

$$3MgO + 2Al \longrightarrow 3Mg + Al_2O_3$$
  
 $3MgO + CaC_2 \longrightarrow 3Mg + CaO + 2CO$ 

The reduction is done at 2000°C in vacuum. The vapours of magnesium are condensed.

(ii) Electrolysis of anhydrous magnesium chloride: Carnallite (KCl·MgCl $_2$ ·6H $_2$ O) is a hydrated compound. It cannot be dehydrated by heating because the water of crystallisation reacts chemically with magnesium chloride to form magnesium oxychloride and finally magnesium oxide.

$$\begin{array}{c} MgCl_2 \cdot 6H_2O \xrightarrow{Heated} MgCl_2 \cdot 2H_2O \xrightarrow{Heated} \\ Hexahydrate & Dihydrate \\ \hline \\ Mg_2OCl_2 \xrightarrow{Strongly} MgO \\ Oxychloride & heated in air \end{array}$$

To make it anhydrous, it is first heated in air and then in a current of HCl gas.

Anhydrous magnesium chloride can also be obtained from MgO or sea water. Chlorine is passed over red hot mixture of MgO and carbon.

$$MgO + C + Cl_2 \longrightarrow MgCl_2 + CO$$

Sea water contains magnesium compounds. It is treated with calcium hydroxide when magnesium hydroxide gets precipitated. It is dissolved in dilute HCl. The solution is then concentrated when hydrated magnesium chloride crystallises out. It is dehydrated as described above.

$$\begin{array}{c} \text{Mg}^{2+} + \text{Ca}(\text{OH})_2 & \longrightarrow & \text{Mg}(\text{OH})_2 + \text{Ca}^{2+} \\ \text{(Sea water, MgCl}_2 \text{ or MgSO}_4) & \text{ppt.} \\ \\ \text{Mg}(\text{OH})_2 + 2\text{HCl} & \longrightarrow & \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \\ \\ \text{MgCl}_2 \cdot 6\text{H}_2\text{O} & \xrightarrow{\text{Heated}} & \text{MgCl}_2 + 6\text{H}_2\text{O} \\ \hline \\ \text{HCl}(g) & \text{Anhydrous} \end{array}$$

Finally, the magnesium chloride is dried. The anhydrous magnesium chloride is fused with NaCl and anhydrous calcium

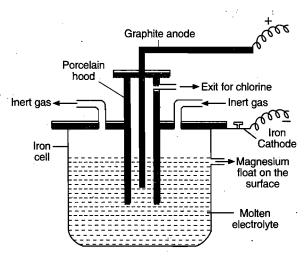


Fig. 7.3 An electrolytic cell

chloride in the ratio of 35% (MgCl<sub>2</sub>); 50% (NaCl) and 15% (CaCl<sub>2</sub>). The mixture is electrolysed at 700°C in presence of an inert gas in an electrolytic cell as shown in Fig. 7.3.

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Magnesium being lighter than the fused mass floats on the surface from where it is removed periodically by perforated ladles.

The purpose of addition of NaCl and CaCl<sub>2</sub> to anhydrous MgCl<sub>2</sub> is to lower the fusion temperature and make the fused mass good conductor of electricity.

## **Properties**

**Physical Properties:** Magnesium is a silvery-white metal. It is a light metal. It is fairly hard and is malleable and ductile. Its great advantage is its low density (1.74 g/cm<sup>3</sup>), which is only two-thirds that of aluminium 2.70 g/cm<sup>3</sup>. It is sold in the form of ribbons or wire. It melts at 650°C. It is good conductor of heat and electricity.

Chemical Properties: (i) Reaction with air: Pure magnesium metal is a relatively reactive element. It is not affected by dry air. It is slowly tarnished in moist air.

Once magnesium metal has been ignited, it burns vigorously in air to form the oxide with bright white light forming a dense smoke.

$$2Mg + O_2 \longrightarrow 2MgO$$

$$3Mg + N_2(Air) \longrightarrow Mg_3N_2$$

(ii) Reaction with water: Magnesium is not affected by cold water. It decomposes steam or boiling water with evolution of hydrogen.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

(iii) Reaction with acids: It displaces hydrogen from dilute acids.

 $Mg + 2HCl \longrightarrow MgCl_2 + H_2$ 

$$\begin{array}{cccc} Mg + H_2SO_4 & \longrightarrow & MgSO_4 + H_2 \\ Mg + 2HNO_3 & \longrightarrow & Mg(NO_3)_2 + H_2 \\ \end{array}$$
 With hot concentrated  $H_2SO_4$ , it evolves  $SO_2$ .
$$\begin{array}{cccc} H_2SO_4 & \longrightarrow & H_2O + SO_2 + O \\ Mg + O & \longrightarrow & MgO \end{array}$$

$$\frac{\text{MgO} + \text{H}_2\text{SO}_4 \longrightarrow \text{MgSO}_4 + \text{H}_2\text{O}}{\text{Mg} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{MgSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}}$$

(iv) Reaction with halogens: Magnesium on heating with halogens, readily form halides.

$$Mg + X_2 \longrightarrow MgX_2$$
(X may be F, Cl, Br or I)

(v) Reducing property: Magnesium acts as a strong reducing agent as it has great affinity for oxygen at high temperature. It even burns in the atmosphere of CO<sub>2</sub>, CO, SO<sub>2</sub>, NO, etc.

$$2Mg + CO_2 \longrightarrow 2MgO + C$$
  
 $2Mg + SO_2 \longrightarrow 2MgO + S$   
 $5Mg + 2NO \longrightarrow 2MgO + Mg_3N_2$ 

It reduces oxides of metals and non-metals

$$B_2O_3 + 3Mg \longrightarrow 3MgO + 2B$$

With KClO<sub>3</sub>, it burns with explosion

$$3Mg + KClO_3 \longrightarrow 3MgO + KCl$$

(vi) Formation of Grignard reagent: Magnesium dissolves in ether solution of alkyl halides and forms organometallic compounds known as Grignard reagents. These reagents are used in organic synthesis.

$$Mg + RI \longrightarrow Mg \stackrel{R}{\swarrow}$$

Alkyl magnesium iodide

(vii) Displacement reactions: Since, magnesium is highly electropositive metal, it displaces less electropositive metals from their salts solutions.

$$Mg + 2AgNO_3 \longrightarrow Mg(NO_3)_2 + 2Ag$$

(viii) Reaction with FeCl<sub>3</sub> or  $NH_4Cl$  solution: Magnesium dissolves in FeCl<sub>3</sub> or  $NH_4Cl$  solution with evolution of hydrogen.

$$[FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl] \times 2$$

$$[Mg + 2HCl \longrightarrow MgCl_2 + H_2] \times 3$$

$$3Mg + 2FeCl_3 + 6H_2O \longrightarrow 3MgCl_2 + 2Fe(OH)_3 + 3H_2$$

$$Mg + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_3 + H_2$$

## Uses

- (i) It is used for the extraction of boron and silicon.
- (ii) Magnesium ribbon alongwith barium peroxide is used as ignition mixture in aluminothermite process.
- (iii) Magnesium powder mixed with potassium chlorate is used in flash bulbs for photography.
  - (iv) It is used for making Grignard reagents.
- (v) It is employed as a deoxidiser in metallurgy and for the removal of last traces of air from radio-valves.
- (vi) Large quantities of magnesium oxide are used in animal feed supplements because magnesium ion is an important nutrient for animals. The ion is also important for human nutrition.
- (vii) Magnesium metal is also used as a reducing agent in the manufacture of titanium and zirconium from their tetrachlorides.

$$ZrCl_4 + 2Mg \longrightarrow Zr + 2MgCl_2$$

(viii) Most commercial aluminium metal contains some percentage of magnesium, which improves the hardness and corrosion resistance of the aluminium.

(ix) Its alloys, however, contain aluminium and small quantities of other metals to impart both strength and corrosion resistance. Magnesium alloys are used to make automobile, aircraft parts, as well as power-tools. The important alloys are:

Magnalium 95% Al Used in the construction of airships, 5% Mg balances and pistons of motor engines. Electron metal 95% Mg 4.5% Zn Used in the construction of air-crafts. 0.5% Cu 95% Al Duralumin Its strength and toughness is comp-0.5% Mg arable with mild steel. It is used for 0.5% Mn making airships. 4% Cu

## COMPOUNDS OF MAGNESIUM

## 1. Magnesium Oxide, MgO, (Magnesia)

**Preparation:** It can be prepared by following reactions.

$$2Mg + O_{2} \xrightarrow{Burning} 2MgO$$

$$Mg(OH)_{2} \xrightarrow{Heated} MgO + H_{2}O$$

$$2Mg(NO_{3})_{2} \xrightarrow{Heated} 2MgO + 4NO_{2} + O_{2}$$

$$MgCO_{3} \xrightarrow{Heated} MgO + CO_{2}$$

**Properties:** It is a light infusible white powder. It fuses at 2800°C. It is quite stable at high temperature and is a good thermal insulator. It is slightly soluble in water and forms magnesium hydroxide.

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

It is basic in nature. It reacts with acids to form corresponding salts.

$$\begin{array}{ccc} MgO + 2HCl & \longrightarrow & MgCl_2 + H_2O \\ MgO + H_2SO_4 & \longrightarrow & MgSO_4 + H_2O \end{array}$$

It is reduced by carbon at very high temperature.

$$MgO + C \longrightarrow Mg + CO$$

Magnesium oxide when mixed with a saturated solution of magnesium chloride sets to a hard mass like cement known as **magnesia cement** or **Sorel cement**. The composition is MgCl<sub>2</sub>·5MgO·xH<sub>2</sub>O.

Uses: It is used:

- (i) in medicine as antacid.
- (ii) refractory bricks for furnaces.
- (iii) as an insulator when mixed with asbestos for lagging steam pipes and boilers.
- (iv) as an adsorbent in the manufacture of dynamite and in the vulcanization of rubber.
- (v) for making Sorel cement which is employed in dental filling, in cementing glass and porcelain, in plaster casting, etc.

## ■ 2. Magnesium Hydroxide, Mg(OH)<sub>2</sub>

**Preparation:** It is prepared by dissolving magnesium oxide in water or by treating magnesium salt with an alkali.

$$\begin{array}{ccc} MgO + H_2O & \longrightarrow & Mg(OH)_2 \\ MgCl_2 + Ca(OH)_2 & \longrightarrow & Mg(OH)_2 + CaCl_2 \\ MgCl_2 + 2NaOH & \longrightarrow & Mg(OH)_2 + 2NaCl_2 \end{array}$$

**Properties:** It is a white powder. It is sparingly soluble in water. It is basic in nature and forms salts with acids. It decomposes on heating. It readily dissolves in strong solution of  $NH_4Cl$ .

$$Mg(OH)_2 + 2NH_4Cl \iff MgCl_2 + 2NH_4OH$$

Uses: A suspension of Mg(OH)<sub>2</sub> in water is used in medicine as an antacid under the name, *milk of magnesia*, because the magnesium hydroxide reacts to neutralize excess of hydrochloric acid present in the stomach.

## 3. Magnesium Carbonate, MgCO<sub>3</sub>

It is found in nature as magnesite (MgCO<sub>3</sub>) and dolomite (MgCO<sub>3</sub>·CaCO<sub>3</sub>).

**Preparation:** It can be prepared by adding sodium bicarbonate to a hot solution of magnesium salt.

$$MgSO_4 + 2NaHCO_3 \longrightarrow MgCO_3 + Na_2SO_4 + H_2O + CO_2$$

The magnesium carbonate cannot be obtained by the addition of sodium carbonate to the solution of magnesium salt. A white precipitate of a basic carbonate of composition  $3MgCO_3 Mg(OH)_2 3H_2O$  is obtained. It is known as **magnesia alva.** It is suspended in water and  $CO_2$  is passed when magnesium bicarbonate known as **fluid magnesia** is formed.

The solution is boiled when normal magnesium carbonate separates out.

$$2MgSO_4 + 2Na_2CO_3 + H_2O \longrightarrow \\ MgCO_3 \cdot Mg(OH)_2 + 2Na_2SO_4 + CO_2 \\ MgCO_3 \cdot Mg(OH)_2 + 3CO_2 + H_2O \longrightarrow 2Mg(HCO_3)_2 \\ Mg(HCO_3)_2 \longrightarrow MgCO_3 + CO_2 + H_2O$$

**Properties:** It is a white powder, insoluble in water. It dissolves readily in water containing excess of carbon dioxide.

$$MgCO_3 + CO_2 + H_2O \longrightarrow Mg(HCO_3)_2$$

It dissolves in acids forming salts with evolution of CQ2.

$$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2$$

$$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + H_2O + CO_2$$

On heating, it decomposes with evolution of CO2.

$$MgCO_3 \longrightarrow MgO + CO_2$$

It forms double carbonates with alkali carbonates.

$$MgCO_3 + Na_2CO_3 \longrightarrow Na_2Mg(CO_3)_2$$
  
Soluble

Uses: It is used:

(i) as a filler for paper, rubber and pigments.

- (ii) in the form of basic magnesium carbonate (magnesia alva) for making tooth powders, cosmetics and in medicine as antacid.
  - (iii) in the form of magnesite as a refractory material.
  - (iv) in glass manufacture, ceramics and inks.

## 4. Magnesium Chloride, MgCl<sub>2</sub>.6H<sub>2</sub>O

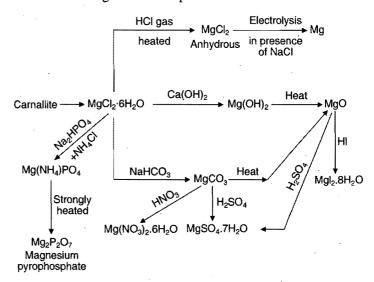
It occurs as mineral carnallite, KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O and bischofite, MgCl<sub>2</sub>·H<sub>2</sub>O. It is found in sea water, mineral springs, etc.

**Preparation:** (a) It is extracted from carnallite mineral. The mineral is fused and cooled to 176°C when whole of KCl is deposited while MgCl<sub>2</sub>·6H<sub>2</sub>O remains in the fused state.

(b) It can also be obtained by dissolving Mg, MgO,Mg(OH)<sub>2</sub> or MgCO<sub>3</sub> in dilute hydrochloric acid.

The preparation of anhydrous magnesium chloride has already been described in the extraction of magnesium.

**Properties:** It is a colourless crystalline solid, highly deliquescent and highly soluble in water. It is the starting material for various magnesium compounds.



Uses: It is used:

- (i) for making Mg, MgO and other magnesium compounds.
- (ii) for making Sorel cement.
- (iii) in lubrication of cotton threads for spinning.
- (iv) in the preparation of **xylotite** which is used as covering for floors, laboratory tables, etc.

## ■ 5. Magnesium Sulphate, MgSO<sub>4</sub>·7H<sub>2</sub>O

It occurs in nature as minerals kieserite (MgSO<sub>4</sub>·H<sub>2</sub>O), epsom salt (MgSO<sub>4</sub>·7H<sub>2</sub>O) and kainite (KCl·MgSO<sub>4</sub>·3H<sub>2</sub>O).

**Preparation:** It is formed by reacting magnesite (MgCO<sub>3</sub>) or dolomite with dilute sulphuric acid.

$$\begin{array}{c} MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2 \\ MgCO_3 \cdot CaCO_3 + 2H_2SO_4 \rightarrow MgSO_4 + CaSO_4 + 2CO_2 + 2H_2O \\ \text{Dolomite} & \text{(Insoluble)} \end{array}$$

It is commercially prepared by boiling kieserite mineral in water. The crystals are obtained when the solution is cooled.

$$MgSO_4 \cdot H_2O + 6H_2O \longrightarrow MgSO_4 \cdot 7H_2O$$

**Properties:** It is a colourless crystalline compound, soluble in water. The crystals are efflorescent and bitter in taste. It is isomorphous with ZnSO<sub>4</sub>·7H<sub>2</sub>O. It forms double sulphates with alkali metal sulphates, K<sub>2</sub>SO<sub>4</sub>·MgSO<sub>4</sub>·6H<sub>2</sub>O (Schonite).

**Heating effect:** When heated to 150°C, it changes to monohydrate. On further heating, it becomes anhydrous at 200°C. On strong heating, it decomposes into MgO.

$$MgSO_4 \cdot 7H_2O \xrightarrow{150^{\circ}C} MgSO_4 \cdot H_2O \xrightarrow{200^{\circ}C} MgSO_4 \xrightarrow{Strong} MgO + SO_2 + \frac{1}{2}O_2$$

Magnesium sulphate is reduced by lampblack at 800°C.

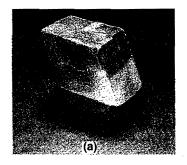
$$2MgSO_4 + C \longrightarrow 2MgO + 2SO_2 + CO_2$$

Uses: It is used:

- (a) as fertilizer.
- (b) as a laxative and analgesic in medicine.
- (c) as a filler for paper.
- (d) as a mordant in dyeing and tanning industry.
- (e) in the manufacture of paints and soaps and in fire-proofing fabrics.

### 7.7 CALCIUM

**Occurrence:** Calcium is a common element. In the combined state it is widely distributed in nature. Calcium is a rather abundant element specially in the form of its carbonate, CaCO<sub>3</sub>. This single compound takes on many different forms in nature appearing as chalk, limestone, marble, or crystalline **calcite** and **aragonite** under different geological circumstances.



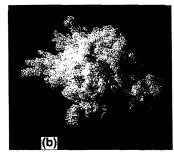


Fig. 7.4 Calcium carbonate (CaCO<sub>3</sub>) occurs in two crystalline forms: calcite (a) and aragonite (b). Limestone is an aggregate of small crystals

It is present in the earth's crust as silicates, which weather to give free calcium ion Ca<sup>++</sup>. The ion is about as abundant in sea water as magnesium ions. Calcium ion is an important nutrient for living organisms. Seashells are principally calcium carbonate. Corals are marine organisms that grow in colonies;

their calcium carbonate skeletons eventually form enormous coral reefs in warm water. It occurs as:

- (i) Carbonate—Limestone, marble, chalk, iceland spar and calcite as CaCO<sub>3</sub> and dolomite as MgCO<sub>3</sub>·CaCO<sub>3</sub>.
- (ii) Sulphate—Gypsum  $CaSO_4 \cdot 2H_2O$  and anhydrite  $CaSO_4$ .
  - (iii) Fluoride—Fluorspar CaF<sub>2</sub>,

Fluorapatite 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·CaF<sub>2</sub>.

(iv) Phosphate—Phosphorite Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

It is present in natural water and causes hardness in water. It is an essential constituent of bones and teeth. Egg and seashells contain calcium carbonate.

**Extraction:** Calcium is obtained by electrolysis of a fused mass consisting six parts calcium chloride and one part calcium fluoride at about 700°C in an electrolytic cell made of graphite which acts as anode and a water cooled cathode of iron which is suspended from the top in the fused mass. On passing current, calcium is discharged at cathode. It gets solidified as cathode is water cooled.

 $CaCl_2 \Longrightarrow Ca^{2+} + 2Cl^{-}$ At anode:  $2Cl^{-} \longrightarrow Cl_2 + 2e$ At cathode:  $Ca^{2+} + 2e \longrightarrow Ca$ 

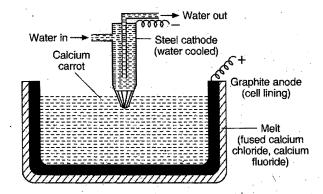


Fig. 7.5 Electrolytic extraction of calcium

Since metallic calcium is soluble in fused CaCl<sub>2</sub> at electrolysis temperature, it should be removed as soon as it is deposited. This is achieved by raising the cathode during electrolysis so that only the extreme tip of the deposited cathode remains in contact with the fused CaCl<sub>2</sub>.

[Note: Na or K is obtained by doing electrolysis of fused NaOH or KOH respectively but calcium cannot be obtained in the same manner as Ca(OH)<sub>2</sub> decomposes into CaO (quick lime) which is difficult to fuse.]

**Properties:** (i) It is a silvery white metal. It is malleable and ductile. It is good conductor of heat and electricity. Its specific gravity is 1.5.

(ii) On exposure, it is covered with a white powder consisting  $Ca(OH)_2$  and  $Ca_3N_2$ . It burns in air forming quick lime (CaO) and calcium nitride ( $Ca_3N_2$ ). It decomposes water evolving hydrogen.

$$2Ca + O_2 \longrightarrow 2CaO$$
  
 $3Ca + N_2 \longrightarrow Ca_3N_2$ 

Calcium reacts gently with water at room temperature to produce hydrogen and calcium hydroxide.

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

(iii) It has affinity for non-metals.

$$\begin{array}{c} 2\text{Ca} + \text{O}_2 \longrightarrow 2\text{CaO} \text{ (Calcium oxide)} \\ \text{Ca} + \text{H}_2 \stackrel{\text{Heat}}{\longrightarrow} \text{CaH}_2 \text{ (Calcium hydride)} \\ \text{Ca} + \text{Cl}_2 \stackrel{\text{Heat}}{\longrightarrow} \text{CaCl}_2 \text{ (Calcium chloride)} \\ \text{Ca} + 2\text{C} \stackrel{\text{Heat}}{\longrightarrow} \text{CaC}_2 \text{ (Calcium carbide)} \\ 3\text{Ca} + \text{N}_2 \stackrel{\text{Heat}}{\longrightarrow} \text{Ca}_3\text{N}_2 \text{ (Calcium nitride)} \\ \text{Ca} + \text{S} \longrightarrow \text{CaS} \text{ (Calcium sulphide)} \\ \end{array}$$

- (iv) It reacts violently with acids evolving hydrogen.
- (v) It reduces many metal oxides.

$$Cr_2O_3 + 3Ca \longrightarrow 2Cr + 3CaO$$
  
 $V_2O_5 + 5Ca \longrightarrow 2V + 5CaO$ 

(vi) When heated in atmosphere of CO<sub>2</sub>, it forms calcium carbide and calcium oxide.

$$5Ca + 2CO_2 \xrightarrow{Heat} CaC_2 + 4CaO$$

(vii) It dissolves in liquid ammonia. On evaporation, calcium ammoniate is formed.

$$Ca + 6NH_3 \longrightarrow Ca(NH_3)_6$$

On heating Ca(NH<sub>3</sub>)<sub>6</sub>, calcium amide is first formed which then changes into nitride.

$$Ca(NH_3)_6 \xrightarrow{\text{Heat}} Ca(NH_2)_2 + 4NH_3 \uparrow + H_2 \uparrow$$

$$3Ca(NH_2)_2 \xrightarrow{\text{Heat}} Ca_3N_2 + 4NH_3$$

Uses: (i) It is used as a deoxidiser for copper, cast iron and steel.

- (ii) It removes sulphur during petroleum refining.
- (iii) The metal is used in preference to sodium for the removal of last traces of water from alcohol as it does not react with alcohol.
  - (iv) It is also used as a reducing agent.

### COMPOUNDS OF CALCIUM

### 1. Quick Lime, CaO

Limestone, CaCO<sub>3</sub> found in nature is the starting material of almost all the compounds of calcium. Calcium oxide (CaO) is also called **quick lime** or **burnt lime**. It is obtained on large scale by heating limestone (CaCO<sub>3</sub>) in specially designed kilns (Fig. 7.6). The decomposition of calcium carbonate is a reversible process.

$$CaCO_3 \Longrightarrow CaO + CO_2$$

The reaction moves towards right hand direction if  $\rm CO_2$  formed is immediately removed from the kiln by allowing a blast of air to enter the kiln through fire boxes. The temperature for the decomposition of limestone should be near about  $\rm 1000^{\circ}C$  otherwise at higher temperature, the clay present in the limestone as impurity will react with it to form silicate.

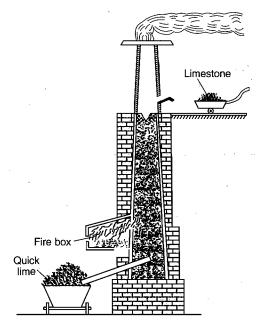


Fig. 7.6 Continuous vertical lime kiln with separate feed

Calcium oxide is a white amorphous solid. It is the cheapest form of alkali. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
  
 $CaO + CO_2 \longrightarrow CaCO_3$ 

Being basic in nature, it combines with acidic oxides at high temperature.

$$\begin{array}{c} \text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3 \\ \text{6CaO} + \text{P}_4\text{O}_{10} \longrightarrow \text{2Ca}_3(\text{PO}_4)_2 \end{array}$$

### Slaked lime, $Ca(OH)_2(s)$ and lime water, $Ca(OH)_2(aq)$

Lime is sparingly soluble in water. When water is added to lime, a hissing sound is produced alongwith clouds of steam. In this process a large amount of heat energy is given out. The lime cracks with the formation of a powder called **slaked lime**  $[Ca(OH)_2]$ .

$$CaO + H_2O \longrightarrow Ca(OH)_2 + Heat energy$$
Ouick lime Slaked lime

The process is known as **slaking of lime**. The paste of lime in water is called **milk of lime** while the filtered and clear solution is known as **lime water**. Chemically both are Ca(OH)<sub>2</sub>.

$$\begin{array}{c} \text{Limestone} \xrightarrow{1000^{\circ}\text{C}} \text{Quick lime} \xrightarrow{\text{H}_2\text{O}} \text{Slaked lime} \\ & (\text{CaO}) & & [\text{Ca}(\text{OH})_2] \\ & & \downarrow \\ & & \text{Suspension} \longleftarrow \text{Suspended in water} \\ & & (\text{Milk of lime}) & & \downarrow \text{Filter} \\ & & \text{Ca}(\text{OH})_2 & & \text{Clear solution} \\ & & & (\text{Lime water}) \\ & & & \text{Ca}(\text{OH})_2 & & \\ \end{array}$$

**Properties:** It is a white amorphous powder and is sparingly soluble in water. When  $CO_2$  is passed through lime water, it turns milky due to the formation of calcium carbonate. On passing excess of  $CO_2$ , the precipitate dissolves forming calcium bicarbonate,  $Ca(HCO_3)_2$ .

$$\begin{array}{c} \text{Ca(OH)}_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O} \\ \text{Insoluble} \\ \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow \text{Ca(HCO}_3)_2 \\ \text{Soluble} \end{array}$$

This reaction, with its formation of milky precipitate, is the basis of a simple test for carbon dioxide.

It reacts with Cl<sub>2</sub> to form bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow \underbrace{CaCl_2 + Ca(OCl)_2}_{Bleaching powder} + 2H_2O$$
or
$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$
Bleaching powder

### **■** Uses

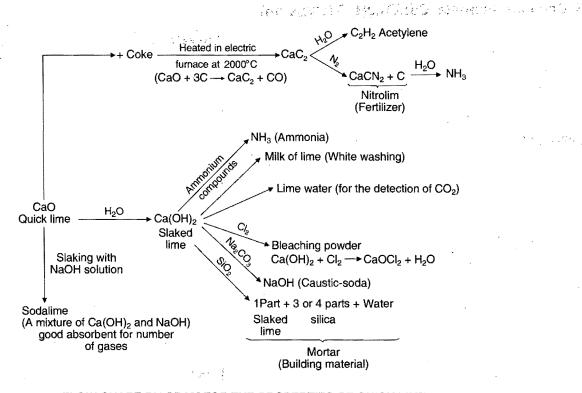
Quick lime is a commercial compound being used in various chemical industries as caustic soda, in the purification of sugar, manufacture of dye stuffs, bleaching powder, calcium carbide, calcium salts, mortar, cement, glass, etc.

Other uses of quick lime: (i) As it has high melting point (2600°C), it is used for furnace linings.

(ii) It is used as a basic flux in metallurgy as it combines with acidic impurities.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

- (iii) It is used as a disinfectant and germicide, as a drying agent for ammonia and alcohol.
- (iv) It is employed for the purification of coal gas and softening of water.
- (v) In the construction of buildings slaked lime is mixed with three to four times its weight of sand. The mixture is made into a thick paste with gradual addition of water. This paste is called **brick laying mortar** and is used in building construction. It sets to a hard mass by loss of water and gradual absorption of CO<sub>2</sub> from the air. Sometimes coal ash is mixed with lime instead of sand. A mortar obtained from hydraulic lime is called **hydraulic mortar**. It has greater strength and is used for construction of bridges.



Birth Small at a

### FLOW CHART DIAGRAM FOR THE PROPERTIES OF QUICK LIME

### 2. Calcium Carbonate, CaCO<sub>3</sub>

Limestone is one of the most important raw material for the chemicals and building industries. It is found in nature in huge quantities in various forms such as limestone, marble, chalk, etc.

Infact calcium carbonate is the second most abundant material in the earth's crust after silicate like clay, sand and sandstone.

Chalk is the softest form of calcium carbonate. Deposits of chalk have formed from the shells of dead sea creations that lived million of years ago. In some places the chalk covered with other rocks and put under great pressure. This changed the soft chalk into harder **rock-limestone**. In other places the chalk was under pressure and heat. This changed the soft chalk into **marble**, the hardest form of calcium carbonate.

It can be obtained by passing carbon dioxide through lime water or by adding sodium carbonate solution to CaCl<sub>2</sub>.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
  
 $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$ 

The precipitate of CaCO<sub>3</sub> thus obtained is known as **precipitated chalk**, a pure form of the finely divided compound.

It is a white powder, insoluble in water. It dissolves in presence of CO<sub>2</sub> due to formation of calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

- **Uses:** (i) Precipitated chalk is used in tooth pastes, tooth powders, and face powders, in medicine for indigestion, in adhesives in cosmetics and as a filler for paper.
  - (ii) Chalk is used in paints and distempers.
- (iii) Marble is used, (a) for building purposes, (b) in the production of CO<sub>2</sub> in laboratory.
- (iv) Limestone is used, (a) in the manufacture of quick lime, slaked lime, cement, washing soda and glass, (b) as a flux in the smelting of iron and lead ores.

### 3. Calcium Sulphate, CaSO<sub>4</sub>.2H<sub>2</sub>O (Gypsum)

It is found in nature as anhydride (CaSO<sub>4</sub>) and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O).

It can be prepared by reacting any calcium salt with either sulphuric acid or a soluble sulphate.

$$CaCl_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HCl$$
  
 $CaCl_2 + Na_2SO_4 \longrightarrow CaSO_4 + 2NaCl$ 

**Properties:** (i) It is a white crystalline solid. It is sparingly soluble in water and solubility decreases as temperature increases.

- (ii) It dissolves in dilute acids. It also dissolves in ammonium sulphate due to the formation of double sulphate,  $(NH_4)_2SO_4\cdot CaSO_4\cdot H_2O$ .
- (iii) Gypsum when heated first changes from monoclinic form to orthorhombic form without loss of water. At 120°C, it loses three-fourth of its water of crystallisation and forms hemihydrate, (2CaSO<sub>4</sub>·H<sub>2</sub>O) which is commonly known as **plaster of Paris.** At 200°C, it becomes anhydrous. The anhydrous form is known as **burnt plaster** or **dead plaster**.

$$\begin{split} 2[\text{CaSO}_4\text{·}2\text{H}_2\text{O}] &\xrightarrow{-120^{\circ}\text{C}} \quad [2\text{CaSO}_4\text{·}\text{H}_2\text{O}] + \quad 3\text{H}_2\text{O} \\ [2\text{CaSO}_4\text{·}\text{H}_2\text{O}] &\xrightarrow{-200^{\circ}\text{C}} \quad 2\text{CaSO}_4 + \quad \text{H}_2\text{O} \end{split}$$

When strongly heated, it decomposes to give calcium oxide.

$$\begin{array}{c} 2\text{CaSO}_4 \xrightarrow{\text{Strongly}} 2\text{CaO} + 2\text{SO}_2 + \text{O}_2 \\ \\ \text{CaSO}_4.2\text{H}_2\text{O} \xrightarrow{\text{Heated}} \text{CaSO}_4.2\text{H}_2\text{O} \xrightarrow{\text{120°C}} 2\text{CaSO}_4.\text{H}_2\text{O} \xrightarrow{\text{200°C}} \text{CaSO}_4 \\ \\ \text{Gypsum} \\ \text{(monoclinic)} & \text{(Orthorhombic)} & \text{Plaster of Paris} & \text{Anhydrous} \\ \\ \text{(burnt plaster)} & \text{Strongly} \\ \text{heated} & \text{O}_2 + \text{SO}_2 + \text{CaO} & \text{(lime)} \\ \end{array}$$

(iv) A suspension of gypsum when saturated with ammonia and carbon dioxide forms ammonium sulphate, a nitrogenous fertilizer.

$$2NH_3 + CaSO_4 + CO_2 + H_2O \longrightarrow (NH_4)_2SO_4 + CaCO_3$$

(v) When strongly heated with carbon, it forms calcium sulphide.

$$CaSO_4 + 4C \longrightarrow CaS + 4CO$$

Uses: It is used:

- (i) for the manufacture of plaster of Paris, cement, ammonium sulphate, sulphuric acid, etc.
  - (ii) for preparing blackboard chalk.
  - (iii) in anhydrous form as drying agent.

### 4. Plaster of Paris, 2CaSO<sub>4</sub>.H<sub>2</sub>O

(Calcium sulphate hemihydrate)

**Preparation:** It is obtained when gypsum, calcium sulphate dihydrate (CaSO<sub>4</sub>·2H<sub>2</sub>O), is heated at 120°C.

$$\begin{array}{cccc} 2[CaSO_4 \cdot 2H_2O] & \longrightarrow & 2CaSO_4 \cdot H_2O + 3H_2O \\ Calcium & sulphate & dihydrate & Calcium & sulphate \\ & & & & & hemihydrate \\ & & & & (Plaster of Paris) \end{array}$$

Properties: (i) Plaster of Paris is a white powder.

(ii) It has the property of setting to a hard mass when a paste with water is allowed to stand aside for sometime. Slight expansion occurs during the setting as water is absorbed to reform CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum). The setting process is exothermic. The process of setting takes place in two stages. In the first stage, there is conversion of plaster of Paris into orthorhombic form of gypsum (setting step) and in the second stage orthorhombic form changes into monoclinic form (hardening step).

$$2CaSO_4 \cdot H_2O \xrightarrow[H_2O]{Setting} CaSO_4 \cdot 2H_2O \xrightarrow[M_2O]{Hardening} CaSO_4 \cdot 2H_2O$$
Plaster of Paris Orthorhombic Monoclinic

The setting of plaster of Paris may be catalysed by sodium chloride while it is retarded by borax or alum. Addition of alum to plaster of Paris makes the setting very hard. The mixture is known as **Keene cement.** 

(iii) When plaster of Paris is heated at 200°C, it forms anhydrous calcium sulphate which is known as **dead plaster**. It has no setting property as it takes up water only very slowly.

Uses: It is used:

- (i) in surgery for setting broken or dislocated bones.
- (ii) in making casts for statues, toys, surgical instruments, etc.
  - (iii) in making casts in dentistry.
  - (iv) in making blackboard chalk.

### 3 4. Portland Cement

Portland cement is one of the most important building materials at the present time. It is used in the construction of buildings, roads, bridges, dams, etc. It was discovered, in 1824, by an English Mason, Joseph Aspdin who observed that when strongly heated mixture of limestone and clay was mixed with water and allowed to stand, it hardened to a stone-like mass which resembled portland rock—a famous building stone of England. Since then the name **portland cement** has been given to a mixture containing high percentage of lime with silica, iron oxide, alumina, etc.

Cement is a dirty greyish heavy powder containing calcium aluminates and silicates. The silicates and aluminates which form more than 90% of the cement are:

(i) Tricalcium silicate	3CaO·SiO <sub>2</sub>
(ii) Dicalcium silicate	2CaO⋅SiO <sub>2</sub>
(iii) Tricalcium aluminate	3CaO·Al <sub>2</sub> O <sub>3</sub>
(iv) Tetracalcium alumino-ferrite	4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub>

Of these, tricalcium silicate is most important.

**Composition of portland cement :** The approximate composition of portland cement is given below:

Oxide		Percentage by mass
Lime (Calcium oxide)	(CaO)	61.69%
Silica	(SiO <sub>2</sub> )	18.24%
Alumina	(Al <sub>2</sub> O <sub>3</sub> )	4-8%
Ferric oxide	$(Fe_2O_3)$	1-8%
Minor oxides	(MgO, Na <sub>2</sub> O, K <sub>2</sub> O, SO <sub>3</sub> )	2-4%

The essential constituents are lime, silica and alumina. These are generally kept in the following ratio:

$$\frac{\% \text{ Silica}}{\% \text{ Al}_2 \text{O}_3} = 2.5 - 4.0 ;$$

$$\frac{\% \text{ CaO}}{\% \text{ SiO}_2 + \% \text{ Al}_2 \text{O}_3 + \% \text{ Fe}_2 \text{O}_3} = 1.9 - 2.1$$

The cement containing no iron is white.

**Raw materials:** The important raw materials needed for the manufacture of cement are:

- (i) Limestone—This provides lime.
- (ii) Clay-This provides alumina and silica.
- (iii) Gypsum, (CaSO<sub>4</sub>·2H<sub>2</sub>O).

**Manufacture:** There are two processes in use for the manufacture of cement (i) Dry process and (ii) Wet process.

**Dry process:** The process is used when limestone is hard in nature. The limestone is first broken into small pieces. It is then mixed with clay in proper proportions. The mixture is finally pulverised to such an extent that it passes through a 100 mesh sieve. This homogeneous mixture is known as raw meal.

Wet process: The process is used when limestone and clay both are soft in nature. The clay is washed with water in wash mill to remove foreign materials like flint. The powdered limestone is mixed with clay paste in the ratio of 75% (limestone) and 25% (clay). The mixture is finely ground and made homogeneous. The homogeneous paste is known as slurry. It contains 40% (approximately) water.

**Calcination in rotary kiln:** This step is mainly responsible for the formation of cement. The heating of raw meal (dry process) or slurry (wet process) is done in a rotary kiln at a very high temperature 1400–1600°C. The kiln consists of a long cylinder 6 to 10 feet in diameter and 100 to 250 feet in length. It is made of steel and lined inside with fire bricks (Fig.7.7).

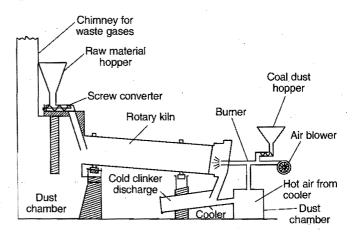


Fig. 7.7

The charge (raw meal or slurry) is introduced in the kiln with the help of a screw conveyer. It moves forward with the rotary motion given to the kiln. The charge is heated by burning coal dust which is blown in from the other side with the help of a blower. In the upper portion of the kiln, the temperature is about 750°C where whole of moisture is eliminated. In the middle portion, the temperature is about 1000°C. The limestone decomposes with evolution of CO<sub>2</sub>. At the lower end, the temperature is 1600°C. The following reactions occur:

$$\begin{array}{c} \text{CaCO}_{3} \longrightarrow \text{CaO} + \text{CO}_{2} \\ 2\text{CaO} + \text{SiO}_{2} \longrightarrow 2\text{CaO} \cdot \text{SiO}_{2} \\ 3\text{CaO} + \text{SiO}_{2} \longrightarrow 3\text{CaO} \cdot \text{SiO}_{2} \\ 3\text{CaO} + \text{Al}_{2}\text{O}_{3} \longrightarrow 3\text{CaO} \cdot \text{Al}_{2}\text{O}_{3} \\ 4\text{CaO} + \text{Al}_{2}\text{O}_{3} + \text{Fe}_{2}\text{O}_{3} \longrightarrow 4\text{CaO} \cdot \text{Al}_{2}\text{O}_{3} \cdot \text{Fe}_{2}\text{O}_{3} \end{array}$$

The product formed is technically called as clinker. It is cooled and mixed with 2 or 3% of its weight of gypsum. It is then ground to an exceedingly fine powder. The powder is packed in air tight bags.

The purpose of the addition of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) is to increase the setting time of the cement.

**Setting of cement:** When cement is mixed with water and left as such for some time, it becomes a hard mass. This is known as setting of cement. The exact mechanism of this setting process is not known. It is believed that various aluminates and silicates present in the cement form hydrates with water which separate in the form of gel.

$$3\text{CaO·Al}_2\text{O}_3 + 6\text{H}_2\text{O} \xrightarrow{\text{Hydration}} 3\text{CaO·Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$$
Colloidal gel

$$\begin{array}{c} 2\text{CaO·SiO}_2 + x\text{H}_2\text{O} \xrightarrow{\text{Hydration}} 2\text{CaO·SiO}_2 \cdot x\text{H}_2\text{O} \\ & \text{Colloidal gel} \\ 4\text{CaO·Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 + 6\text{H}_2\text{O} \xrightarrow{\text{Hydration}} \\ & 3\text{CaO·Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + \text{Fe}_2\text{O}_3 \cdot \text{CaO} \\ & \text{Colloidal gel} \end{array}$$

At the same time some Ca(OH)<sub>2</sub> and Al(OH)<sub>3</sub> are formed as precipitates due to hydrolysis.

$$3\text{CaO·SiO}_2 + \text{H}_2\text{O} \xrightarrow{\text{Hydrolysis}} \text{Ca(OH)}_2 + 2\text{CaO·SiO}_2$$
  
 $3\text{CaO·Al}_2\text{O}_3 + 6\text{H}_2\text{O} \xrightarrow{\text{Hydrolysis}} 3\text{Ca(OH)}_2 + 2\text{Al(OH)}_3$ 

Gypsum combines with tricalcium aluminate to form calcium sulpho-aluminate.

$$3\text{CaO} \cdot \text{A1}_2\text{O}_3 + 3\text{CaSO}_4 + 2\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{A1}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$$

This reaction slows down the setting.

The gels formed start losing water partly by evaporation and partly by forming hydrates with unhydrated constituents. This results in the formation of a hard mass. Ca(OH)<sub>2</sub> binds the particles of calcium silicate together, while Al(OH)<sub>3</sub> fills the interstices resulting in hardening the mass.

Setting of cement is an exothermic process. Hence, cement structures have to be cooled during setting by sprinkling water.

Concrete: A mixture of cement, sand, gravel or small pieces of stone and water is known as concrete. It sets to an exceedingly hard structure. It is mainly used for construction of floors. If the cement concrete is filled in and around a wire netting or skeleton of iron rods and allowed to set, the resulting structure is known as reinforced concrete. These structures have great strength and are used for construction of roofs, bridges, etc.

Cement industry in India: Cement industry was started in India with the establishment of first factory in 1904 in Tamil Nadu. India is, at present, one of top ten cement producing countries in the world. There are about 60 cement factories in public and private sectors producing near about 2.5 crore tons cement annually.

### 7.8 COMPOUNDS OF BARIUM

**Preparation:** Barium is found in nature mainly in the form of sulphate, BaSO<sub>4</sub>, called barytes or heavy spar. Barytes is a source for the preparation of various compounds of barium which are of industrial importance.

The natural barytes is ground, mixed with coke and the mixture is heated in a rotary kiln, barium sulphate is reduced to barium sulphide.

$$BaSO_4 + 4C \longrightarrow BaS + 4CO$$

The kiln clinker is extracted with water. The solution is treated with sodium carbonate to precipitate barium carbonate.

$$BaS + Na_2CO_3 \longrightarrow BaCO_3 + Na_2S$$

Barium carbonate is used further for barium compounds and the filtrate is concentrated for sodium sulphide crystals, Na<sub>2</sub>S·9H<sub>2</sub>O. Barium carbonate cannot be decomposed by heat. It is mixed with carbon and heated in a furnace to form barium oxide.

$$BaCO_3 + C \longrightarrow BaO + 2CO$$

The barium oxide when heated at 540°C in purified air is oxidised to barium peroxide.

$$2BaO + O_2 \xrightarrow{540^{\circ}C} 2BaO_2$$

Barium carbonate is used for the preparation of other salts as acetate, chloride and nitrate.

$$BaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ba + CO_2 + H_2O$$

$$BaCO_3 + 2HC1 \longrightarrow BaCl_2 + CO_2 + H_2O$$

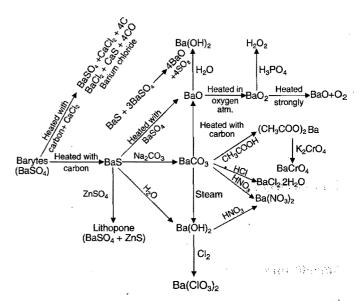
$$BaCO_3 + 2HNO_3 \longrightarrow Ba(NO_3)_2 + CO_2 + H_2O$$

When barium carbonate is heated to red heat in a current of steam, barium hydroxide is formed with evolution of carbon dioxide.

$$BaCO_3 + H_2O \longrightarrow Ba(OH)_2 + CO_2$$

Barium chlorate, Ba(ClO<sub>3</sub>)<sub>2</sub> can be prepared by the action of chlorine on barium hydroxide solution (hot and concentrated). Barium chlorate being less soluble, separates out.

$$6Ba(OH)_2 + 6Cl_2 \longrightarrow Ba(ClO_3)_2 + 5BaCl_2 + 6H_2O$$



Uses: Uses of barium compounds:

- (i) BaO is an excellent drying agent especially for organic bases like pyridine.
- (ii)  $BaO_2$  is used in the preparation of  $H_2O_2$  and ignition mixture used in thermite process. It is also used as an oxidising agent.
- (iii) Ba(OH)<sub>2</sub> is used for the preparation of a standard alkali solution for titrating acids.
- (iv) BaCl<sub>2</sub> is used as a laboratory reagent for the test of sulphate radical.
- (v) Ba(ClO<sub>3</sub>)<sub>2</sub> is used for producing green fire and for the preparation of chloric acid.

- (vi) BaSO<sub>4</sub> is used as a white pigment either as such or mixed with zinc sulphide under the name of lithopone (BaSO<sub>4</sub> + ZnS). It is also used as a filler in rubber and paper industry.
- (vii) Barium titanate (BaTiO<sub>3</sub>) is **piezoelectric**, which means that it becomes electrically charged when it is mechanically distorted. This property leads to its use for underwater sound detection, in which a mechanical vibration is converted into an electrical signal.

(viii) When barium hydroxide octahydrate.  $Ba(OH)_2 \cdot 8H_2O$ , and ammonium thiocyanate,  $NH_4SCN$ , are ground together, one moderately, endothermic reaction takes place. An endothermic reaction absorbs heat. The reaction mixture becomes so cold that moisture from the air forms a layer of frost on the outside of the beaker.

 $Ba(OH)_2 \cdot 8H_2O + 2NH_4SCN \longrightarrow Ba(SCN)_2 + 2NH_3 + 10H_2O - Heat$ 

### SOME SOLVED PROBLEMS

### **Example 1.** Explain the following:

(i) Beryllium chloride fumes in air.

or

Beryllium chloride is acidic when dissolved in water.

- (ii) Barium ion,  $Ba^{2+}$ , is poisonous, yet  $BaSO_4$  is given to patients prior to taking stomach X-ray. Why is it safe to use  $BaSO_4$  internally?
- (iii) Alkaline alkali metals.
  - (iv) Alkaline earth metal salts are diamagnetic in nature.
  - (v) Magnesium oxide is used as a refractory material.

#### Solution:

(i) BeCl<sub>2</sub> undergoes hydrolysis being a salt of a weak base and a strong acid. Fumes of HCl gas are evolved in presence of moisture in atmosphere.

or

When dissolved in water, strong acid HCl is formed in solution.

$$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$$

- (ii) BaSO<sub>4</sub> is extremely insoluble and does not pass from digestive system into the circulatory system.
- (iii) Alkaline earth metals have high values of atomisation and ionisation potentials in comparison to alkali metals. The oxidation potentials have lower values than alkali metals and hence, alkaline earth metals are weaker reducing agents.
- (iv) The ions of alkaline earth metals,  $M^{2+}$ , have inert gas configuration, *i.e.*, all the orbitals are doubly occupied.

Hence, alkaline earth metal salts are diamagnetic in nature.

(v) MgO has very high melting point and does not decompose as its lattice energy is very high. It is, thus, used as refractory material.

### **Example 2.** Give reasons for the following:

- (i) Solubility of the sulphates of alkaline earth metals decreases from top to bottom in the group.
- (ii) Solubility of hydroxides of alkaline earth metals increases from top to bottom in the group.
- (iii) Sodium chloride is added during electrolysis of fused anhydrous MgCl<sub>2</sub>.
- (iv) Alkaline earth metal salts are less soluble than the corresponding alkali metal salts.

- (v) Beryllium oxide is insoluble but BaO is soluble.
- (vi) BeCl<sub>2</sub> can be easily hydrolysed.

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### **Solution:**

- (i) Lattice energies of the sulphates are nearly the same. The size of sulphate ion is large and small changes in cation size do not affect the lattice energies. However, the hydration energies decrease from Be<sup>2+</sup> to Ba<sup>2+</sup>. Hence, solubility of sulphates decreases from top to bottom.
- (ii) Lattice energies of hydroxides decrease as the size of cation increases. It overcomes the effect of decrease in hydration energy and hence, the solubility of hydroxides increases from top to bottom.
- (iii) NaCl is added as to lower the fusion temperature of MgCl<sub>2</sub> and to make the mixture as good conductor of electricity.
- (iv) Lattice energies of the salts of alkaline earth metals are very high in comparison to alkali metal salts. High lattice energies are responsible for low solubility.
- (v) The lattice energy of BeO is higher than BaO due to small size of Be<sup>2+</sup> ion. The other reason may be that BeO is covalent and polymeric while BaO is ionic in nature.
- (vi) The Be<sup>2+</sup> ions are easily hydrated because of high charge size ratio. The hydrolysis occurs because Be—O bond is very strong.

**Example 3.** Give the names and formula of the compounds indicated in the following statements:

- (a) A compound of Ca used in setting fractured bones.
- (b) A compound of Mg, S, O and H used as a purgative in medicine.
- (c) A compound of Ca and C used for the production of acetylene.
  - (d) A compound of Ca, C and N used as a fertilizer.
- (e) A triatomic compound which on treatment with water gives  $H_2$ .

Solution: (a) Plaster of Paris, 2CaSO<sub>4</sub>·H<sub>2</sub>O

- (b) Magnesium sulphate, MgSO<sub>4</sub>·7H<sub>2</sub>O
- (c) Calcium carbide, CaC<sub>2</sub>

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

- (d) Calcium cyanamide (nitrolim), CaCN<sub>2</sub>
- (e) Calcium hydride (hydrolith), CaH2

**Example 4.** 0.3 g of magnesium ribbon was placed in a crucible and heated with the lid on until the magnesium began to burn brilliantly. At the end of the experiment there was 0.45 g of the white powder left. Show that this result does not agree with the equation,

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

What might have gone wrong?

**Solution:** The given equation is,

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$
  
2×24=48 g 2×(24+16)=80 g

The equation shows that 48 g of magnesium should give 80 g of magnesium oxide. Therefore, 0.3 g of magnesium should give  $\frac{80 \times 0.3}{48} = 0.5$  g of the oxide. The actual amount of MgO obtained is 0.45 g. Perhaps some of the oxide escaped as smoke or the magnesium did not react completely or the magnesium may have combined with nitrogen to make magnesium nitride instead.

**Example 5.** Beryllium gives a compound with the following percentage composition: Be, 6.1%; N, 37.8%; Cl, 48%; H, 8.1%. One mole of the compound had a mass of 148 g. M(Be) = 9 g  $mol^{-1}$ .

- (i) What is the molecular formula of the compound?
- (ii) In water, 1 mole of the compound reacts with 2 moles of  $Ag^+$  ions.

Suggest a structural formula for the compound.

#### Solution:

Determination of empirical formula

Element	Percentage	At. mass	Relative number atom	Simplest ratio
Be	6.1	9.0	$\frac{6.1}{9} = 0.68$	$\frac{0.68}{0.68} = 1$
N	37.8	14.0	$\frac{37.8}{14} = 2.7$	$\frac{2.7}{0.68} = 4$
Cl	48.0	35.5	$\frac{48.0}{35.5} = 1.35$	$\frac{1.35}{0.68} = 2$
Н	8.1	1.0	$\frac{8.1}{1.0} = 8.1$	$\frac{8.1}{0.68} = 12$

Empirical formula =  $BeN_4Cl_2H_{12}$ 

Empirical mass =  $9 + 4 \times 14 + 2 \times 35.5 + 12 \times 1 = 148$ Hence, molecular formula = BeN<sub>4</sub>Cl<sub>2</sub>H<sub>12</sub>

The reaction with silver ions suggests that 2 chlorine atoms are present as chloride ions. Thus, the structural formula of the compound is [Be(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>.

**Example 6.** Compare the thermal stability of the following compounds of the alkali metals with those of alkaline earth metals: (a) nitrates (b) carbonates (c) sulphates.

#### **Solution:**

(a) Nitrates: Nitrates of both alkali and alkaline earth metals decompose on heating.

Nitrates of alkali metals decompose to form metal nitrites and  $O_2$ .

$$2MNO_3 \longrightarrow 2MNO_2 + O_2$$
 (M = Na, K, Rb or Cs)

Nitrates of alkaline earth metals decompose forming corresponding metal oxides, NO<sub>2</sub> and O<sub>2</sub>.

$$M(NO_3)_2 \longrightarrow MO + 2NO_2 + O_2$$
  
(M = Be, Mg, Ca, Sr or Ba)

Lithium nitrate behaves like Mg(NO<sub>3</sub>)<sub>2</sub> due to diagonal relationship.

$$4\text{LiNO}_3 \longrightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$$

**(b) Carbonates:** Carbonates of alkali metals are stable and do not decomposes on heating.

Carbonates of alkaline earth metals decompose on heating. However, stability increases as the decomposition temperature indicate which increase from BeCO<sub>3</sub> to BaCO<sub>3</sub>.

$$MCO_3 \longrightarrow MO + CO_2$$

Li<sub>2</sub>CO<sub>3</sub> like MgCO<sub>3</sub> also decomposes on heating.

$$\text{Li}_2\text{CO}_3 \longrightarrow \text{Li}_2\text{O} + \text{CO}_2$$

**(c) Sulphates:** Sulphates of alkali metals are stable and do not decompose on heating.

Sulphates of alkaline earth metals decompose on heating into oxides and SO<sub>3</sub>.

$$MSO_4 \longrightarrow MO + SO_3$$

The stability increases as the temperature of decomposition of these sulphates increase gradually.

Li<sub>2</sub>SO<sub>4</sub> like MgSO<sub>4</sub> also decomposes on heating.

**Example 7.** (a) Why  $BaSO_4$  is insoluble whereas  $BeSO_4$  is soluble in water?

(b) What is the hybrid state of Be in BeCl<sub>2</sub>? What will be the change in the hybrid state of BeCl<sub>2</sub> in the solid state?

[C.B.S.E. (P.M.T.) 2005]

#### **Solution:**

- (a) The lattice energy of BaSO<sub>4</sub> is much more than its hydration energy and hence it is insoluble in water. The hydration energy of BeSO<sub>4</sub> is much higher than its lattice energy because of small size of Be<sup>2+</sup> ions. Hence, it is soluble in water.
- (b) In the vapour state,  $BeCl_2$  is linear as Be is sp hybridized. However, in solid state,  $BeCl_2$  is polymeric. In the polymeric structure, each Be has two covalent and two co-ordinate bonds, *i.e.*, Be is  $sp^3$  hybridized.
- **Example 8.** (a)  $Mg_3N_2$  when reacted with water gives off ammonia but HCl is not obtained when  $MgCl_2$  reacts with water at room temperature. Give reason.
- (b) Chlorination of calcium hydroxide produces bleaching powder. Write the chemical equation.

#### **Solution:**

(a) Mg<sub>3</sub>N<sub>2</sub> is a salt of a strong base, Mg(OH)<sub>2</sub>, and a weak acid (NH<sub>3</sub>) and hence gets hydrolysed to give NH<sub>3</sub>.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

MgCl<sub>2</sub> is a salt of a strong base and a strong acid (HCl) and hence, its hydrolysis does not occur.

$$\begin{array}{c} \text{(b)} \quad \text{Ca(OH)}_2 + \text{Cl}_2 & \longrightarrow \text{Ca(OCl)Cl} + \text{H}_2\text{O} \\ & \text{Slaked} & \text{Bleaching} \\ & \text{lime} & \text{powder} \end{array}$$

Bleaching powder is also considered as a mixture of Ca(OCl)<sub>2</sub>, CaCl<sub>2</sub> and Ca(OH)<sub>2</sub>.

$$3Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 \cdot Ca(OH)_2 \cdot CaCl_2 \cdot 2H_2O$$
Bleaching powder

**Example 9.** Draw the structure of (i) BeCl<sub>2</sub> (vapour state) (ii) BeCl<sub>2</sub> (solid).

#### Solution.

In vapour state, it has chlorobridged dimer structure which dissociates into linear monomer at 1000°C.

In the solid state, it has a polymeric structure with dichlorobridges in which a halogen atom bonded to one beryllium atom uses a lone pair of electrons to form a co-ordinate bond to other beryllium atom.

**Example 10.** (a) Halides of Be dissolve in organic solvents while those of barium do not. Why is it so?

- (b) What is the difference between milk of lime and lime water?
- (c) Why is calcium preferred over sodium to remove last traces of moisture from alcohol?

### Solution.

- (a) Halides of beryllium are covalent due to small size of Be<sup>2+</sup> ion while halides of barium are ionic.
- (b) The suspension of Ca(OH)<sub>2</sub> in water is termed milk of lime while clear solution of Ca(OH)<sub>2</sub> is called lime water.
- (c) Both Ca and Na can remove moisture from alcohol but sodium reacts with alcohol also readily. Calcium reacts with alcohol very slowly.

**Example 11.** (a) State any one reason for alkaline earth metals, why they have a greater tendency to form complexes than alkali metals.

(b) Alkaline earth metals cannot be obtained by chemical reduction.

#### Solution.

- (a) Alkaline earth metal cations have smaller size and higher charge in comparison to alkali metal cations. These factors are responsible for greater tendency to form complexes.
- (b) Alkaline earth metals cannot be obtained by chemical reduction as they themselves are stronger reducing agents than common reducing agents. With carbon, they form carbides.

### Example 12. How would you explain?

- (i) BeO is insoluble but BeSO<sub>4</sub> is soluble in water.
- (ii) BaO is soluble but BaSO<sub>4</sub> is insoluble in water.
- (iii) What is the difference between milk of lime and lime water?
  - (iv) Why do halides and hydrides of beryllium polymerise? Solution.
- (i) The lattice enthalpy of BeO is higher than its hydration enthalpy and thus it is insoluble in water. BeSO<sub>4</sub> on the other hand has lower lattice enthalpy than hydration enthalpy and hence it is soluble in water. The lower lattice enthalpy is due to bigger size of  $SO_4^{2-}$  ion.
- (ii) In BaO, the lattice enthalpy is less than hydration enthalpy and thus it is soluble in water while in BaSO<sub>4</sub>, the lattice enthalpy is more than hydration enthalpy and hence, it is insoluble in water.
- (iii) Both milk of lime and lime water are chemically same *i.e.*, Ca(OH)<sub>2</sub>. The suspension of slaked lime in water is called milk of lime while clear solution of slaked lime is know as lime water. Slaked lime is sparingly soluble in water.
- (iv) The monomeric molecules BeH<sub>2</sub> and BeCl<sub>2</sub> formed with normal bonds will result in only four electrons in the outer shell of beryllium atom making it electron deficient. By polymerising, each atom shares its electrons with several neighbours and receives a share in their electrons making the situation more favourable. Therefore, the halides and hydrides of Be polymerise.

### O

### SUMMARY AND IMPORTANT POINTS TO REMEMBER

- IIA group of the periodic table consists of six elementsberyllium, magnesium, calcium, strontium, barium and radium. These elements are called alkaline earth metals. The oxides of these elements are alkaline and exist in the earth-so they are called alkaline earth metals. The last member is radioactive.
- The first element, beryllium, is less active than other elements and shows abnormal properties like lithium in IA group on account of small atomic and ionic size and high electronegativity. It shows resemblance with aluminium (an element of IIIrd group), i.e., diagonal relationship.
- 3. The outermost shell of these elements has two electrons, *i.e.*,  $ns^2$  configuration. Because of their similarity in electronic configuration [noble gas]  $ns^2$ , they are included in the same group and closely resemble each other. There is a gradual gradation in their properties from top to bottom as atomic number increases.

#### 4. Physical characteristics

(i) All are silvery white metals. They are soft but harder than alkali metals. Softness increases from Be to Ba.

16. Plaster of Paris has the property of setting to a hard mass—CaSO<sub>4</sub>·2H<sub>2</sub>O, slight expansion occurs during setting. Addition of alum to plaster of Paris makes the setting very hard. The mixture is known as **Keene cement.** 

Plaster of Paris is used for setting broken or dislocated bones, casts for statues, toys and in dentistry.

When plaster of Paris is heated at 200°C, it forms anhydrous calcium sulphate which is known as **dead plaster**. It has no setting property.

- 17. (a) Anhydrous CaCl<sub>2</sub> is a good drying agent. It cannot be used for drying ammonia and alcohol as it forms addition products with them.
  - (b) Hydroxyapatite, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub> OH is the main component of tooth enamel. Cavities are formed when acids decompose this enamel. This can be prevented by converting the hydroxyapatite to more resistant enamel–fluorapatite, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>·F.
  - (c) Most of the kidney stones consist of calcium oxalate, CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O.
  - (d) Mg<sup>2+</sup> and Ca<sup>2+</sup> ions present in water are responsible for hardness of water.
  - (e) CaC<sub>2</sub> is obtained by heating a mixture of CaO and carbon. It reacts with nitrogen forming nitrolim, used as a fertilizer.

$$CaC_2 + N_2 \longrightarrow \underbrace{CaCN_2 + C}_{\text{nitrolim}}$$

18. Cement is an important building material. The average composition of portland cement is: CaO 61.5%, SiO<sub>2</sub> 22.5%, Al<sub>2</sub>O<sub>3</sub> 7.5%. Cement is a dirty greyish heavy powder containing calcium silicates and aluminates. Cement consists of:

Tricalcium silicate 3CaO·SiO<sub>2</sub>

Dicalcium silicate 2CaO·SiO<sub>2</sub>

Tricalcium aluminate 3CaO · Al<sub>2</sub>O<sub>3</sub>

Tetracalcium alumino-ferrite 4CaO·Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>

For manufacture, limestone and clay are fused at 1400–1600°C in a rotary kiln. The product obtained is called **clinker.** It is mixed with 2–3% gypsum and powdered.

When cement is mixed with water, it sets to a hard mass, this is called setting. Setting is an exothermic process. During setting hydration occurs.

- **19.** Be shows diagonal relationship with aluminium, the second element of III A group.
  - (a) The polarising power of Be<sup>2+</sup> and Al<sup>3+</sup> ions is high. Consequently the compounds are covalent.
  - (b) The electronegativity of both the elements is nearly the same.
  - (c) Both do not decompose water.
  - (d) Both become passive when treated with conc. HNO<sub>3</sub>.
  - (e) Both dissolve in caustic alkalies liberating H<sub>2</sub>.
  - (f) The oxides and hydroxides are amphoteric.
  - (g) Be<sub>2</sub>C and Al<sub>4</sub>C<sub>3</sub> on hydrolysis evolve CH<sub>4</sub>.
  - (h) Both combine with nitrogen.
  - (i) Both form polymeric hydrides.
  - (j) Halides are formed in similar fashion.

Oxide + C + 
$$Cl_2 \longrightarrow Chloride$$

Halides except fluorides are covalent in nature.

**20.** Solutions of beryllium salts are acidic and dissolve appreciable quantities of Be(OH)<sub>2</sub>. In alkali solution [Be(OH)<sub>4</sub>]<sup>2-</sup> is formed.

$$\begin{split} \left[ \text{Be}(\text{H}_2\text{O})_4 \right]^{2+} & \rightleftharpoons \left[ \text{Be}(\text{H}_2\text{O})_3(\text{OH}) \right]^+ + \text{H}^+ \\ \left[ \text{Be}(\text{H}_2\text{O})_3(\text{OH}) \right]^+ & \rightleftharpoons \left[ \text{Be}(\text{H}_2\text{O})_2(\text{OH})_2 \right] + \text{H}^+ \\ \left[ \text{Be}(\text{H}_2\text{O})_2(\text{OH})_2 \right] & \rightleftharpoons \left[ \text{Be}(\text{H}_2\text{O})(\text{OH})_3 \right]^- + \text{H}^+ \\ \left[ \text{Be}(\text{H}_2\text{O})(\text{OH})_3 \right]^- & \rightleftharpoons \left[ \text{Be}(\text{OH})_4 \right]^{2-} + \text{H}^+ \end{split}$$

- 21. SrCO<sub>3</sub> is used in the manufacture of glass for colour TV picture tube.
- 22. BaSO<sub>4</sub> is used in medicine as a contrast medium for stomach and intestinal X-rays.

### - • • • - PRACTICE PROBLEMS - • • • -

### **■** Subjective Type Questions

#### 1. Give reasons:

- (a) Halides of Beryllium are soluble in organic solvents.
- (b) Beryllium chloride fumes in moist air.
- (c) CaCO<sub>3</sub> dissolves in water in excess of CO<sub>2</sub>.
- (d) A piece of burning magnesium ribbon continues to burn in SO<sub>2</sub>.
- (e) CaCl<sub>2</sub> cannot be used for drying ammonia.

### 2. Answer the following:

- (i) Name three natural forms of calcium carbonate.
- (ii) Which alkaline earth metal is found in abundance in earth's crust?
- (iii) Name the alkaline earth metal which is radioactive in nature.
- (iv) Name the natural carbonate mineral in which both calcium and magnesium are present.

- (v) Name two ores of magnesium.
- (vi) Which element of alkaline earth metal has least density?
- (a) Name the element which is invariable bivalent and whose oxide is soluble in excess of NaOH.
  - (b) Name the alkaline earth metal which shows resemblance with aluminium.
  - (c) Name the alkaline metal hydroxide which is amphoteric.
  - (d) Which elements of group 2 do not give characteristic flame colouration?
  - (e) Which out of Mg<sup>2+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup> has maximum ionic mobility?
  - (f) What is dead burnt plaster?
  - (g) What is fly ash?
- 4. Give the name and formula of the compounds as indicated in the following statements:
  - A compound of calcium and hydrogen which is used as a portable source of hydrogen for filling balloons.

- (ii) A compound of Mg, O, Cl and H used as a cement for joining cracked teeth.
- (iii) A compound of Ca, O, Cl and H used as a germicide.
- (iv) A compound of Mg, Cl and O used as drying agent.
- (v) A compound of Ca and O which when heated in oxycoal gas flame gives lime light.
- 5. How do the following properties of the alkaline earth metals change when we move from Be to Ba?
  - Size of the atoms and ions
  - (ii) Ionisation energies
- (iii) Electronegativity
- (iv) Hardness
- (v) Oxidation potential
- (vi) Basic character of hydroxides
- (vii) Solubility of hydroxides (viii) Solubility of sulphates
- (ix) Stability of carbonates
- (x) Reducing nature
- **6.** Write the chemical formula of the following:
  - (a) Quick lime
- (b) Slaked lime
- (c) Anhydrone

- (d) Baryta water
- (e) Marble
- (f) Anhydrite

- (g) Gypsum
- (h) Plaster of Paris
- (i) Asbestos

- (j) Hydrolith.
- 7. Write formulae of the following minerals:
  - (i) Beryl, (ii) Magnesite, (iii) Kieserite, (iv) Witherite,
  - (v) Celestine, (vi) Epsom salt, (vii) Chrysoberyl, (viii) Baryta,
  - (ix) Strontianite, (x) Fluorspar.
- **8.** What happen when the following are heated?
  - (i) Hydrated magnesium chloride, (ii) Gypsum, (iii) Bicarbonates of alkaline earth metals, (iv) Epsom salt, (v) Barium nitrate.
- **9.** What is the action of water on the following?
  - (i) Beryllium carbide, (ii) Calcium carbide, (iii) Calcium nitride, (iv) Calcium cyanamide, (v) Hydrolith.
- 10. What happens when?
  - (i) Magnesium is burnt in air and the products treated
  - (ii) Water is added, to CaC<sub>2</sub> and the resulting gas is passed through dilute H<sub>2</sub>SO<sub>4</sub> containing HgSO<sub>4</sub>.
  - (iii) Hydrated magnesium chloride is heated in presence of ammonium chloride.
  - (iv) FeCl<sub>3</sub> is treated with magnesium.
  - (v) NH<sub>4</sub>Cl is heated with magnesium.
  - (vi) CO<sub>2</sub> is passed through lime water.
  - (vii) SO<sub>2</sub> is passed through lime water.
  - (viii) Cl<sub>2</sub> reacts with slaked lime under different conditions.
- 11. Complete and balance the following equations:
  - (a)
  - (b)
  - (c)
  - $BaCO_3 + H_2O(steam) \xrightarrow{Heat} \dots + CO_2$
  - (e)  $BeCl_2 + LiAlH_4 \longrightarrow ..... + LiCl + .....$
  - (f) CaO + C  $\xrightarrow{\text{High temp.}} \dots + \text{CO} \xrightarrow{\text{High temp.}} \dots + \dots$
- 12. How will you prepare the following? Give chemical equations also:
  - (a) Bleaching powder from CaCO<sub>3</sub>.
  - (b) Calcium sulphate from CaCO<sub>3</sub>.

- (c) Calcium nitrate from calcium sulphate.
- (d) Anhydrous MgCl<sub>2</sub> from hydrated magnesium chloride.
- (e) Plaster of Paris from gypsum.
- 13. Arrange the following:
  - (i) Mg<sup>2+</sup>, Sr<sup>2+</sup>, Be<sup>2+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup> ions in the increasing order of their heats of hydration.
  - (ii) CaI<sub>2</sub>, CaF<sub>2</sub>, CaCl<sub>2</sub> and CaBr<sub>2</sub> in order of decreasing melting points.
  - (iii) CaCl<sub>2</sub>, BeCl<sub>2</sub>, MgCl<sub>2</sub>, BaCl<sub>2</sub> and SrCl<sub>2</sub> in order of decreasing ionic character.
  - (iv) MgO, SrO, K<sub>2</sub>O and Cs<sub>2</sub>O in order of increasing basic character. [I.J.T. 1991]
  - (v) CaSO<sub>4</sub>, BaSO<sub>4</sub> and MgSO<sub>4</sub> in order of decreasing solubility in water.
  - (vi) BeCO<sub>3</sub>, MgCO<sub>3</sub>, CaCO<sub>3</sub> and BaCO<sub>3</sub> in order of increasing stability.
  - (vii) Sr, Ba, Ca, Mg in order of increasing reducing nature.
  - (viii) BeSO<sub>4</sub>, MgSO<sub>4</sub>, CaSO<sub>4</sub>, SrSO<sub>4</sub> in order of decreasing [I.I.T. 1997] thermal stability.
- **14.** Answer with giving reason:
  - (i) Which are more electropositive alkali metals or alkaline earth metals?
  - (ii) Which one is a covalent hydride?

BeH2, NaH, CaH2

(iii) Which is more hydrated?

(iv) The solution of which one is acidic?

(v) Which has least hardness?

Na, Be, Li, Ca

(vi) Which has the maximum lattice energy?

(vii) Which one are strong reducing agents?

Alkali metals or alkaline earth metals.

- 15. Describe the preparation, properties and uses of the following compounds:
  - (i) Slaked lime
- (ii) Plaster of Paris
- (iii) Calcium carbide
- (iv) Calcium cyanamide
- (v) Magnesium chloride
- (vi) Magnesium sulphate
- **16.** (a) How can magnesium be extracted from magnesite?
  - (b) How can magnesium be extracted from sea water?
  - (c) How various compounds of barium are obtained from barytes?
  - (d) How portland cement is manufactured?
  - (e) How metal calcium is manufactured?
- 17. Explain the following:
  - (i) Magnesium oxide is used for lining of steel making furnace.

[Hint: MgO is a basic flux and helps in the removal of acidic impurities from steel through slag formation.

$$Si + O_2 \longrightarrow SiO_2;$$
  $MgO + SiO_2 \longrightarrow MgSiO_3$ 

$$4P + 5O_2 \longrightarrow P_4O_{10}; 6MgO + P_4O_{10} \longrightarrow 2Mg_3(PO_4)_2$$
  

$$S + O_2 \longrightarrow SO_2; \qquad MgO + SO_2 \longrightarrow MgSO_3]$$

(ii) Anhydrous calcium sulphate (anhydrite) cannot be used as plaster of Paris.

[Hint: Anhydrous calcium sulphate in presence of water does not set like plaster of Paris. However, it is directly changed to gypsum.]

(iii) Anhydrous magnesium chloride is prepared by heating MgCl<sub>2</sub>·6H<sub>2</sub>O in a current of HCl.

[Hint: Magnesium chloride undergoes hydrolysis with its own water of crystallisation. This hydrolysis is prevented in presence of HCl.]

(iv) The reaction between marble and dilute H<sub>2</sub>SO<sub>4</sub> is not used to prepare carbon dioxide.

[Hint: Insoluble CaSO<sub>4</sub> is formed which deposits on the surface of marble and prevents further action of dilute H<sub>2</sub>SO<sub>4</sub>, so the evolution of CO<sub>2</sub> ceases after some-

(v) Lime water becomes turbid on passing CO<sub>2</sub> through it, but becomes clear when more CO<sub>2</sub> is passed.

[Hint: Insoluble CaCO<sub>3</sub> is first precipitated which dissolves in excess of CO<sub>2</sub> in the form of Ca(HCO<sub>3</sub>)<sub>2</sub>.

$$\begin{array}{ccc} \text{Ca(OH)}_2 + \text{CO}_2 & \longrightarrow & \text{CaCO}_3 + \text{H}_2\text{O}; \\ & & \text{(Insoluble)} \\ \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 & \longrightarrow & \text{Ca(HCO}_3)_2] \\ & & & \text{(Soluble)} \end{array}$$

(vi) In the manufacture of Mg by carbon reduction of MgO, the product is cooled in the stream of an inert gas.

[Hint: The reduction of MgO is a reversible process. In order to prevent the reaction between Mg and CO, the temperature of the products is reduced in a stream of an inert gas. Inert gas does not permit the reaction of Mg with air.

$$MgO + C \iff Mg + CO$$

(vii) Magnesium metal burns in air to give a white ash. When this ash is treated with water, the odour of ammonia can be detected. What is the reason? [B.I.T. 1990]

**Hint:** The white ash consists small amount of magnesium nitride which is formed along with MgO when Mg burns in air. Magnesium nitride is hydrolysed with water and NH<sub>3</sub> is evolved.]

(viii) The first ionisation potential of alkaline earth metals is low and hence they should prefer to form  $M^+$  ions. In fact they form  $M^{2+}$  ions.

**Hint:**  $M^{2+}$  ions are extensively hydrated to form hydrated ions and a large amount of energy is released. This energy more than counter balances the higher value of second ionisation energy.]

(ix) Alkaline earth metals have higher melting points than alkali metals.

[Hint: Metallic bonding is much stronger in alkaline earth metals as two electrons are present in valence shell.]

(x) Why gypsum is added to cement?

**Hint:** The purpose of adding gypsum is to increase the setting time of the cement.]

(xi) Beryllium sulphate is soluble but BaSO<sub>4</sub> is insoluble.

[Hint: Because of high hydration energy of beryllium ion, its sulphate is soluble. Barium being a larger cation has much lower hydration energy.]

(xii) Beryllium does not exhibit a covalency beyond 4.

[Hint: The outermost energy shell in beryllium is the second. It cannot accommodate more than 8 electrons and hence a covalency limit 4 cannot be exceeded.]

(xiii) The crystalline salts of alkaline earth metals contain more water of crystallisation than the corresponding alkali metal salts. Why? H.I.T. 19971

[Hint: The ionic radii of alkaline earth metal ions are smaller than alkali metal ions.]

18. Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes milky on bubbling carbon dioxide. Identify A, B, C and D. [I.I.T. 1997]

[Hint: The element A is calcium.

### Matching Type Questions

#### Match the following:

[A] (a) Anhydrite

(b) Carnallite

(c) Dolomite

(d) Epsomite

(e) Fluorapatite

[B] (a) Gypsum

(b) Hydrolith

(c) Marble

(d) Bone ash

(e) Slaked lime

(f) Quick lime

[C] (a) Nitrolim

(b) Green flame

(c) Brick red flame

(d) Asbestos

(e) Electron

(f) Sorel cement

(i) CaSO<sub>4</sub>

(ii) KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O

(iii) MgSO<sub>4</sub>·7H<sub>2</sub>O

(iv) Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·CaF<sub>2</sub>

(v) MgCO<sub>3</sub>·CaCO<sub>3</sub>

(i) CaH<sub>2</sub>

(ii) CaO

(iii) Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>

(iv) CaSO<sub>4</sub>·2H<sub>2</sub>O

(v) CaCO<sub>3</sub>

(vi) Ca(OH)2

(i) Calcium salts

(ii) CaMg<sub>3</sub>(SiO<sub>4</sub>)<sub>4</sub>

(iii) MgCl<sub>2</sub>·5MgO·xH<sub>2</sub>O

(iv) 95% Mg, 5% Zn

(v)  $CaCN_2 + C$ 

(vi) Barium salts

### Answers

### Answers: Subjective Type Questions

- 1. (a) Beryllium halides are somewhat covalent in nature.
  - (b) Beryllium chloride undergoes hydrolysis. HCl is given out.

$$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$$

(c) CaCO3 is converted into soluble calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

(d) Mg reacts with SO2 forming MgO and S.

$$2Mg + SO_2 \longrightarrow 2MgO + S$$

(e) CaCl2 reacts with ammonia.

$$CaCl_2 + 8NH_3 \longrightarrow CaCl_2 \cdot 8NH_3$$
Addition product

- 2. (i) (a) Limestone (b) Chalk (c) Marble
  - (ii) Calcium (iii) Radium (iv) Dolomite
  - (v) Magnesite, Epsom salt (vi) Calcium
- 3. (a) Be; BeO dissolved in NaOH
  - (b) Be (c) Be(OH)<sub>2</sub> (d) Be and Mg (e)  $Ba^{2+}$
  - (f) Anhydrous calcium sulphate (CaSO<sub>4</sub>)
  - (g) It is a waste product from steel industry and has properties similar to cement. It mainly consists calcium silicate.
- 4. (i) Calcium hydride, CaH<sub>2</sub>, (ii) Sorel cement, MgCl<sub>2</sub>·5MgOxH<sub>2</sub>O,
  - (iii) Bleaching powder, CaOCl<sub>2</sub>·H<sub>2</sub>O, (iv) Anhydrone, Mg(ClO<sub>4</sub>)<sub>2</sub>.

[Hint: It has strong affinity for water giving Mg(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O.

It loses whole of water when heated at 250°C and drying property is regenerated.]

- (v) Calcium oxide, CaO.
- 5. (i) increases, (ii) decreases, (iii) decreases, (iv) decreases,
  - (v) increases, (vii increases, (viii) decreases,
  - (ix) increases, (x) increases.
- **6.** (a) CaO, (b)  $Ca(OH)_2$ , (c)  $Mg(ClO_4)_2$ , (d)  $Ba(OH)_2$ , (e)  $CaCO_3$ ,
  - (f)  $CaSO_4$ , (g)  $CaSO_4 \cdot 2H_2O$ , (h)  $2CaSO_4 \cdot H_2O$ , (i)  $CaMg_3(SiO_4)_4$ ,
  - (j) CaH<sub>2</sub>.
- 7. (i) 3BeO·Al<sub>2</sub>O<sub>3</sub>·6SiO<sub>2</sub>, (ii) MgCO<sub>3</sub>, (iii) MgSO<sub>4</sub>·H<sub>2</sub>O, (iv) BaCO<sub>3</sub>,
  - (v) SrSO<sub>4</sub>, (vi) MgSO<sub>4</sub>·7H<sub>2</sub>O<sub>7</sub>, (vii) BeO·Al<sub>2</sub>O<sub>3</sub>, (viii) BaSO<sub>4</sub>,
  - (ix)  $SrCO_3$ , (x)  $CaF_2$ .
- 8. (i)  $MgCl_2 \cdot 6H_2O \xrightarrow{Heat} MgCl_2 \cdot 2H_2O \xrightarrow{Heat} Mg(OH)Cl + HCl + H_2O$

1100

#### MgO

(ii)  $CaSO_4 \cdot 2H_2O \xrightarrow{Heat} CaSO_4 \cdot 2H_2O \xrightarrow{120^{\circ}C} 2CaSO_4 \cdot H_2O$ (Monoclinic) (Orthorhombic) Plaster of Paris

$$CaO + SO_2 + \frac{1}{2}O_2 \xleftarrow{Strongly}_{Heated} \quad CaSO_4 \xleftarrow{Heat}_{Burnt \ plaster}$$

(iii)  $M(HCO_3)_2 \longrightarrow MCO_3 + H_2O + CO_2$ 

- (v)  $Ba(NO_3)_2 \longrightarrow BaO + NO_2 + O_2$
- 9. (i) Methane is evolved. Be<sub>2</sub>C +  $4H_2O \longrightarrow 2Be(OH)_2 + CH_4$ 
  - (ii) Acetylene is evolved.  $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

- (iii) Ammonia is evolved.  $Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$
- (iv) Ammonia is evolved.  $CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$
- (v) Hydrogen is evolved.  $CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$
- 10. (i) Magnesium forms magnesium oxide and magnesium nitride.

$$2Mg + O_2 \longrightarrow 2MgO$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

MgO combines with water very slowly forming magnesium hydroxide. Mg<sub>3</sub>N<sub>2</sub> reacts with water evolving ammonia.

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

(ii) Acetylene is evolved. This is passed through dilute H<sub>2</sub>SO<sub>4</sub> when acetaldehyde is formed.

$$\begin{aligned} &\text{CaC}_2 + 2\text{H}_2\text{O} & \longrightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2 \\ &\text{C}_2\text{H}_2 + \text{H}_2\text{O} & \xrightarrow{\text{H}_2\text{SO}_4} & \text{CH}_3\text{CHO} \end{aligned}$$

(iii) Anhydrous ammonium chloride is obtained.

$$MgCl_2 \cdot 6H_2O + NH_4Cl \longrightarrow MgCl_2 \cdot NH_4Cl \cdot 6H_2O$$

 $\mathsf{MgCl}_2 \cdot \mathsf{NH}_4 \mathsf{Cl} \cdot \mathsf{6H}_2 \mathsf{O} \xrightarrow[-6H_2\mathsf{O}]{\mathsf{Heat}} \mathsf{MgCl}_2 \cdot \mathsf{NH}_4 \mathsf{Cl} \xrightarrow[-6H_2\mathsf{O}]{\mathsf{Heat}} \mathsf{MgCl}_2 + \mathsf{NH}_4 \mathsf{Cl}$ 

(iv) 
$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$
.

$$Mg \,+\, 2HCl \,\longrightarrow MgCl_2 \,+\, H_2$$

(v) 
$$Mg + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_3 + H_2$$

(vi) The solution becomes milky due to formation of CaCO<sub>3</sub>. The solution again becomes colourless in excess of CO<sub>2</sub> as CaCO<sub>3</sub> dissolves in the form of calcium bicarbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

(vii) 
$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O$$

$$CaSO_3 + SO_2 + H_2O \longrightarrow Ca(HSO_3)_2$$

(viii) (a) With cold milk of lime, calcium hypochlorite is formed.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + Ca(ClO)_2 + 2H_2O$$

(b) With hot conc. solution of Ca(OH)<sub>2</sub>, calcium chlorate is formed

$$6Ca(OH)_2 + 3Cl_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$$

(c) With cold solid Ca(OH)2, bleaching powder is formed.

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

11. (a) 
$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow MgCO_3 + CaCO_3 + 2H_2O$$

(b) 
$$MgO + CaC_2 \xrightarrow{Heat} Mg + CaO + 2C$$

- (c)  $Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$
- (d)  $BaCO_3 + H_2O(steam) \longrightarrow Ba(OH)_2 + CO_2$
- (e)  $2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$

(f) 
$$CaO + 3C \longrightarrow CaC_2 + CO$$

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

- 12. (a)  $CaCO_3 \xrightarrow{Heat} CaO \xrightarrow{H_2O} Ca(OH)_2 \xrightarrow{Cl_2} CaOCl_2$ 
  - (b)  $CaCO_3 \xrightarrow{HCl} CaCl_2 \cdot 6H_2O \xrightarrow{Dil. H_2SO_4} CaSO_4 \cdot 2H_2O$
  - (c)  $CaSO_4 \cdot 2H_2O \xrightarrow{Strongly} CaO \xrightarrow{Dil. HNO_3} Ca(NO_3)_2$

- $(d) \quad MgCl_2 \cdot 6H_2O \xrightarrow{\quad HCl \ or \ NH_4Cl \quad \\ \quad heated \quad }$
- (e)  $CaSO_4 \cdot 2H_2O \xrightarrow{Heated at} 2CaSO_4 \cdot H_2O$
- (i)  $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Be^{2+}$ 
  - (ii)  $CaF_2 > CaCl_2 > CaBr_2 > CaI_2$
  - (iii)  $BaCl_2 > SrCl_2 > CaCl_2 > MgCl_2 > BeCl_2$
  - (iv)  $MgO < SrO < K_2O < Cs_2O$
  - (v)  $MgSO_4 > CaSO_4 > BaSO_4$
  - (vi) BeCO<sub>3</sub> < MgCO<sub>3</sub> < CaCO<sub>3</sub> < BaCO<sub>3</sub>
  - (vii) Mg < Ca < Sr < Ba
  - (viii) SrSO<sub>4</sub> > CaSO<sub>4</sub> > MgSO<sub>4</sub> > BeSO<sub>4</sub>
- (i) Alkali metals, low ionisation potential.

- (ii) BeH2, low electronegativity of Be, high ionisation potential.
- (iii) Be<sup>2+</sup>, smallest in size.
- (iv) BeCl<sub>2</sub>, hydrolysis occurs, BeCl<sub>2</sub> +  $2H_2O \rightarrow Be(OH)_2 + 2HCl$
- (v) Na, lowest metallic bonding.
- (vi) MgO, Mg<sup>2+</sup> ion is smallest in size and double the charge in comparison to Li<sup>+</sup> and Na<sup>+</sup> ions.
- (vii) Alkali metals, the values of oxidation potentials are high.

### **Answers:** Matching Type Questions

- [A] (a-i); (b-ii); (c-v); (d-iii); (e-iv)
- [B] (a-iv); (b-i); (c-v); (d-iii); (e-vi); (f-ii)
- [C] (a-v); (b-vi); (c-i); (d-ii); (e-iv); (f-iii)

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

- 1. Amongst the following hydroxides, the one which has lowest value of  $K_{\rm sp}$  at ordinary temperature is?
  - (a)  $Be(OH)_2$
- (b)  $Mg(OH)_2$
- (c) Ca(OH)<sub>2</sub>
- (d) Ba(OH)<sub>2</sub>

Ans. (a)

[Hint: Be(OH)<sub>2</sub> is least soluble in water.]

- Yellow phosphorus on reaction with Ca(OH)<sub>2</sub> gives:
  - (a)  $Ca(H_2PO_4)_2$
- (b)  $Ca(H_2PO_2)_2$
- (c) PH<sub>3</sub>
- (d) both (b) and (c)

Ans. (d)

[Hint:  $8P + 3Ca(OH)_2 + 6H_2O \longrightarrow 3Ca(H_2PO_2)_2 + 2PH_3$ ]

- 3. Slaked lime is obtained when water is added to:
  - (a) CaSO<sub>4</sub>· $\frac{1}{2}$ H<sub>2</sub>O
- (b) CaCl<sub>2</sub>

(c) CaO

(d) CaCO<sub>3</sub>

Ans. (c)

[Hint: The slaked lime is calcium hydroxide. It is obtained when water is added to CaO (Lime).

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
]

- As compared to alkali metals, alkaline earth metals:
  - (a) are more metallic
  - (b) have higher densities
  - (c) are stronger reducing agents
  - (d) have larger atomic radii
  - Ans. (b)
- 5. Which of the following carbides give allylene on hydrolysis?
  - (a) CaC<sub>2</sub>

- (b) Be<sub>2</sub>C
- (c) MgC<sub>2</sub>
- (d)  $Mg_2C_3$

Ans. (d)

[Hint:  $Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3 \longrightarrow C \cong CH$ ]

- 6. Black ash is:
  - (a) CaS + NaHCO<sub>3</sub>
- (b)  $CaSO_4 + Na_2CO_3$
- (c)  $CaSO_4 + NaHCO_3$

- (d)  $CaS + Na_2CO_3$

Ans. (d)

- 7. Metallic magnesium is obtained by:
  - (a) reduction of MgO with coke
  - (b) electrolysis of an aqueous solution of MgCl<sub>2</sub>
  - (c) electrolysis of molten MgCl<sub>2</sub>
  - (d) displacement of magnesium by iron from MgCl<sub>2</sub> solution Ans. (c)
- 8. Among the alkaline earth metals, the element forming predominantly covalent compounds is:
  - (a) barium
- (b) beryllium
- (c) strontium
- (d) calcium

Ans. (b)

[Hint: Be<sup>2+</sup> ion has a small size. It has high polarising power.]

- 9. Magnesium is an important component of which biomolecule occurring extensively in living world?
  - (a) Haemoglobin
- (b) ATP
- (c) Chlorophyll
- (d) Vitamin  $B_{12}$

- Ans. (c)
- 10. The solubilities of carbonates decrease down the magnesium group due to a decrease in:
  - (a) entropy of solution formation
  - (b) lattice energies of solids
  - (c) hydration energies of cations
  - (d) inter-ionic attraction

Ans. (c)

- 11. Several blocks of magnesium are fixed to the bottom of a ship
  - (a) prevent action of water and salt
  - (b) prevent puncturing by under sea rocks
  - (c) keep away the sharks
  - (d) make the ship lighter
- 12. A metal M readily forms water soluble sulphate MSO<sub>4</sub>, water insoluble hydroxide  $M(OH)_2$  and oxide MO which becomes inert on heating. The hydroxide is soluble in NaOH. Then M is:

(a) Be

(b) Mg

(c) Ca

(d) Sr

Ans. (a)

[Hint: BeSO<sub>4</sub> - soluble; Be(OH)<sub>2</sub> - insoluble

 $Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$ 

13. Dead burnt plaster is:

[P.M.T. (Kerala) 2006]

(a) CaSO<sub>4</sub>·2H<sub>2</sub>O

(b) MgSO<sub>4</sub>·7H<sub>2</sub>O

(c)  $CaSO_4 \cdot \frac{1}{2} H_2O$ 

(d) CaSO<sub>4</sub>

Ans. (d)

- **14.** Which of the following statement(s) is/are not true about the diagonal relationship of Be and Al?
  - A. Both react with NaOH to liberate hydrogen
  - B. Their oxides are basic
  - C. They become passive by concentrated HNO<sub>3</sub>
  - D. Their carbides give acetylene on treatment with water
  - (a) Only A

(b) B and C

(c) A and D

(d) B and D

Ans. (d)

[Hint: Their oxides are amphoteric and their carbides give methane on treatment with water.]

- **15.** The correct sequence of increasing covalent character is represented by:
  - (a) BeCl<sub>2</sub> < NaCl < LiCl
- (b) NaCl < LiCl < BeCl<sub>2</sub>
- (c) BeCl<sub>2</sub><LiCl<NaCl
- (d) LiCl < NaCl < BeCl<sub>2</sub>

Ans. (b)

[Hint: The polarizing power of cation increases with decrease in size of cation and increase of charge on the cation.]

16. A solid compound 'X' on heating gives  $CO_2$  gas and a residue. The residue mixed with water forms 'Y'. On passing

an excess of  $CO_2$  through 'Y' in water a clear solution 'Z' is obtained. On boiling 'Z' compound 'X' is reformed. The compound 'X' is:

- (a) Ca(HCO<sub>3</sub>)<sub>2</sub>
- (b) CaCO<sub>3</sub>
- (c) Na<sub>2</sub>CO<sub>3</sub>
- (d) K<sub>2</sub>CO<sub>3</sub>

Ans. (b)

[Hint:

$$\begin{array}{ccc} \text{CaCO}_3 & \longrightarrow & \text{CaO} + \text{CO}_2; \\ `X` & \text{residue} \end{array}$$

$$\text{CaO} + \text{H}_2\text{O} \longrightarrow & \text{Ca(OH)}_2 \end{array}$$

$$Ca(OH)_2 + 2CO_2 \longrightarrow Ca(HCO_3)_2;$$

$$Ca(HCO_3)_2 \xrightarrow{boiling} CaCO_3 + H_2O + CO_2$$
]

- 17. In which of the following, the hydration energy is higher than the lattice energy? [C.B.S.E. 2007]
  - (a) MgSO<sub>4</sub>
- (b) RaSO<sub>4</sub>
- (c) SrSO<sub>4</sub>
- (d) BaSO<sub>4</sub>

Ans. (a)

[Hint: Mg<sup>2+</sup> ion is the smallest and hence has highest hydrationenergy.]

- 18. Be and Al exhibit many properties which are similar. But the two elements differ in: [A.I.E.E.E. 2007]
  - (a) forming covalent bonds
  - (b) forming polymeric hydrides
  - (c) exhibiting maximum covalency in compounds
  - (d) exhibiting amphoteric nature in their oxides Ans. (c)

	(a) ionic nature of BeF <sub>2</sub>		64.	Which of the following it	is least soluble in water?	
	(b) greater hydration energy of Be <sup>2+</sup> ion as compared	l to		(a) BaF <sub>2</sub>	$\Box$ (b) SrF <sub>2</sub>	
	crystal lattice			(c) CaF <sub>2</sub>	$\Box$ (d) MgF <sub>2</sub>	
	(c) covalent nature of BeF <sub>2</sub>		65.	When CaC <sub>2</sub> is heated in	atmospheric nitrogen in ar	n electric
	(d) none of the above			furnace, the compound f		
52.	The order of increasing lattice energy of the follow	ving		(a) Ca(CN) <sub>2</sub>	☐ (b) CaNCN	
	compounds is:			(c) Ca <sub>3</sub> N <sub>2</sub>	☐ (d) CaNC <sub>2</sub>	
	(a) NaCl < CaO < NaBr < BaO		66.	· • • -	owing has the tendency	to form
	(b) NaBr < NaCl < BaO < CaO			covalent compounds?	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	101111
	(c) NaCl < NaBr < BaO < CaO			(a) Calcium	☐ (b) Beryllium	
	(d) NaBr < NaCl < CaO < BaO			(c) Strontium	☐ (d) Magnesium	
53.	$Be(OH)_2$ is:		67.		Mg <sup>2+</sup> ions is higher than	
	(a) acidic		07.	(a) Al <sup>3+</sup>	☐ (b) Be <sup>2+</sup>	
	(c) amphoteric			(c) Na <sup>+</sup>		
54.	Hydrolith is the common name of:		60		(d) none of these	
	(a) NaH		08.		metals dissolves in KOH	with the
	(c) CaO			evolution of hydrogen?		
55.	The salts of which of the following give green colour in	fire	l	(a) Ca	□ (b) Mg	
501	works?		60	(c) Sr	☐ (d) Be	
	(a) Na		09.		is used for taking the X-ra	y spectra
	(c) Ba			of the digestive system?		
56.	Which of the following hydroxides is most stable?			(a) CaSO <sub>4</sub>	☐ (b) BaSO <sub>4</sub>	
50.			70	(c) MgSO <sub>4</sub>	☐ (d) BaCO <sub>3</sub>	
			/0.	The formula of calcium of	*	
<i></i>		لسا	]	(a) Ca(CN) <sub>2</sub>	$\Box  \text{(b) } \text{CaC}_2\text{N}_2$	
57.	When hydrated MgCl <sub>2</sub> ·6H <sub>2</sub> O is strongly heated:	_	7.	(c) CaCN <sub>2</sub>	$\square$ (d) $Ca_3N_2$	
	(a) MgO is formed		/1.	Calcium cyanamide reac	ts with steam to form amm	ionia and
*	(b) Mg(OH) <sub>2</sub> is formed			(-) C-(OID	T 4) C 0	_
	(c) Mg(OH)Cl is formed			(a) Ca(OH) <sub>2</sub>	□ (b) CaO	
	(d) anhydrous MgCl <sub>2</sub> is formed			(c) Ca(HCO <sub>3</sub> ) <sub>2</sub>	☐ (d) CaCO <sub>3</sub>	
58.	On strong heating, gypsum gives:		72.	The mixture of MgCl <sub>2</sub> ar	nd MgO is called:	_
	(a) CaO $\Box$ (b) CaSO <sub>4</sub>			(a) sorel cement		
	(c) $CaSO_4 \cdot \frac{1}{2}H_2O$		,	(b) mixed salt		
59.	The radioactive element X decays to give two inert ga	ases.		(c) portland cement		
	The element is:			(d) magnesium oxychlor		
		_	73.		salts is used for clearing sn	ow from
	,2			roads during winters?		
	(c) $^{234}_{90}$ Th $\Box$ (d) $^{237}_{93}$ Np			(a) CaCl <sub>2</sub>	$\Box$ (b) CaF <sub>2</sub>	브
60.	Which of the following salts on heating gives a mixture	e of	1	(c) MgCl <sub>2</sub>	☐ (d) SrCl <sub>2</sub>	
	two gases?	_	74.		<del>-</del>	
	(a) $Ba(NO_3)_2$ $\Box$ (b) $NaNO_3$			(a) $Ca(OH)_2$	$\Box  \text{(b) Sr(OH)}_2$	
	(c) KNO <sub>3</sub>		l	(c) Ba(OH) <sub>2</sub>	$\square$ (d) Mg(OH) <sub>2</sub>	
61	Gypsum is added to clinker during cement manufacture		75.			_
01.	(a) decrease the rate of setting of cement			(a) $Ca_3Al_2O_6$	$\Box  \text{(b) } \text{Ca}_3 \text{SiO}_3$	
	(b) bind the particles of calcium silicate			(c) Ca <sub>2</sub> SiO <sub>4</sub>	$\Box  (d) \ Ca_3(PO_4)_2$	
	(c) facilitate the formation of colloidal gel		76.		g carbides, on hydrolysi	s, yields
			1	methane?		_
(0	(d) all of the above			(a) $Be_2C$	$\square$ (b) MgC <sub>2</sub>	
62.		sona	l	(c) CaC <sub>2</sub>	$\Box$ (d) Mg <sub>2</sub> C <sub>3</sub>	
	state?		77.		crimson light. It probably of	contained
	(a) BeCl <sub>2</sub>			a salt of:		
	(c) SrCl <sub>2</sub>			(a) Ca	□ (b) Sr	
63.				(c) Ba	□ (d) Mg	
	(a) $MgSO_4$		78.		be obtained by heating MgC	1 <sub>2</sub> .6H <sub>2</sub> O:
	(c) $SrSO_4$ $\square$ (d) $BaSO_4$			(a) until it fuses		
				(b) with lime		

	· ·			
	(c) with coal		92. The right order of the solubility of sulphates of alkaline eart	h
	(d) in a current of dry HCl		metals is:	
79.	Amongst the following hydroxides, the one which has	the	( )	
	lowest value of $K_{\rm sp}$ at ordinary temperature is:		(-)8	
	(a) $Mg(OH)_2$		(),	
	(c) $Ba(OH)_2$		(d) $Mg > Ca > Ba > Be > Sr$	
80.	Compounds of alkaline earth metals are less soluble in w	ater	93. Of the following the commonly used in the laborator	У
	than the corresponding alkali metal salts due to:	_	desiccator is:	
	(a) their high ionisation energy		(-)	
	(b) their low electronegativity		(c) NaCl (d) CaCO <sub>3</sub>	
	(c) their low hydration energy		94. A compound with water gives hissing sound and become	ès
01	(d) their high lattice energy		very hot. It is:	
81.	Which of the following chlorides is covalent?	_	(a) calcium carbonate	
	(a) BaCl <sub>2</sub>		(c) quick lime	
	(c) $CaCl_2$ $\Box$ (d) $BeCl_2$		95. Slaking is the process of adding water to:	
82.	In the reaction, Be + 2NaOH $\longrightarrow$ A + H <sub>2</sub> , A is:		(a) $CaSO_4$	$\supset$
	(a) $Be(OH)_2$		(c) CaCO <sub>3</sub>	
	(c) $Na_2BeO_2$		96. Which of the following is different from other three oxides	<sub>5</sub> ?
83.	Barium burns in excess of oxygen forming:		(a) MgO	
	(a) BaO $\Box$ (b) Ba <sub>2</sub> O <sub>2</sub>		(c) ZnO	
	(c) BaO <sub>2</sub> □ (d) none of these		[Hint: MgO is basic while the other three are amphoteric.]	
84.	Which of the following is barytes water?		97. Magnesium is manufactured by electrolysing fuse	d
	(a) Ca(OH) <sub>2</sub>		magnesium chloride using:	
	(c) Be(OH) <sub>2</sub>		\$-1	
85.	Which of the following represents calcium chlorite?			
oo.	(a) CaClO <sub>2</sub>			
06		<b></b>	98. The most abundant metal present in the human body is:	_
86.	Identify the correct statement:	than		
	(a) Gypsum contains a lower percentage of calcium	шап	(-)	
	plaster of Paris (b) Gypsum is obtained by heating plaster of Paris		99. Soda lime is used extensively in decarboxylation reaction	Ю
			obtain alkanes. Soda lime is:	П
	<ul><li>(c) Plaster of Paris is obtained by hydration of gypsum</li><li>(d) Plaster of Paris is obtained by partial oxidation of gyp</li></ul>			
	(d) Flaster of Fairs is obtained by partial oxidation of gyp	Sum	100. The highly efficient method of obtaining beryllium is:	_
97	The sodium is made by electrolysis of a molten mixtur	ப oof	1	
67.	40% NaCl and 60% CaCl <sub>2</sub> because:	COI		
	(a) CaCl <sub>2</sub> helps in the conduction of electricity			
	(b) Ca <sup>2+</sup> can reduce NaCl to Na			
	(c) Ca <sup>2+</sup> can displace Na from NaCl		101. Which of the following statements is not correct?	
	(d) this mixture has a lower melting point than NaCl		(a) Plaster of Paris is made by heating gypsum to 100°C at	nd
88	Kieserite is an ore of:	L		
00.	(a) Cu		· ·	
	(a) Cu			
80	The metal that is extracted from sea water is:	Ц	(c) Third ionisation energies of alkaline earth metals are ve	
09.	(a) Mg			
	(c) Ca		102. Identify the correct statement:	
90	Ordinary blackboard chalk is made of:			
<i>7</i> 0.	(a) limestone		1 · · · · · =	
	(c) fluorspar		(c) Beryllium hydride and magnesium hydride are covaled	
Q1	The most electropositive amongst the alkaline earth m			
71.	THE HIGH EXCLIPTIONALIVE ATHOUGH THE ATRAITUC CALCULUT	ciais		
			(d) All of these.	
	is;	П		
			103. The compound which is insoluble in dil. HCl is:	

- 11. A sodium salt on treatment with MgCl<sub>2</sub> gives white precipitate on heating. The anion of the sodium salt is:
  - (a) HCO<sub>3</sub>
- (b)  $CO_3^{2^{-}}$

(c)  $SO_4^{2-}$ 

- (d) NO<sub>3</sub>
- $\xrightarrow{\text{Heat}}$  MgCO<sub>3</sub> ] [Hint:  $MgCl_2 + 2NaHCO_3 \longrightarrow Mg(HCO_3)_2$
- 12. Lattice energies of BeF<sub>2</sub>, MgF<sub>2</sub>, CaF<sub>2</sub> and BaF<sub>2</sub> are -2906, -2610, -2459 and -2367 kJ mol<sup>-1</sup> respectively. Hydration energies of Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup> and F are -2494, -1921, -1577, -1305 and -457 kJ mol<sup>-1</sup> respectively. Which of the fluorides is soluble in water?
  - (a) BeF<sub>2</sub>

(b) MgF<sub>2</sub>

(c) CaF<sub>2</sub>

(d) BaF<sub>2</sub>

Г	Ti	nt:

	BeF <sub>2</sub>	MgF <sub>2</sub>	CaF <sub>2</sub>	BaF <sub>2</sub>
Hydration	-2494 + 2× (-457)	-1921 + 2 × (-457)	-1577+2×(-457)	-1305 + 2 × (-457)
energy	= - 3408	= - 2835	= ~ 2491	= - 2219
Latticë energy	2906	- 2610	- 2459	- 2367
ΔH solution	- 3408 - (- 2906) = - 502 kJ mol <sup>-1</sup>	-2835 - (-2610) = $-225 \text{ kJ mol}^{-1}$	-2491 - (-2459) = $-32 \text{ kJ mol}^{-1}$	- 2219 - (- 2367) = 148 kJ mol <sup>-1</sup>

 $\Delta H$  solution is -ve in BeF<sub>2</sub>, hence BeF<sub>2</sub> is easily soluble in water.

- 13. The name and the formula of a compound of Ca, C and N used as a fertilizer is:
  - (a) calcium cyanide, Ca (CN)<sub>2</sub>
  - (b) calcium cyanamide, CaCN<sub>2</sub>
  - (c) calcium cyanide having carbon particles,  $(Ca(CN)_2 + C)$
  - (d) calcium cyanamide plus carbon (nitrolim), ( $CaCN_2 + C$ )
- 14. The name and formula of the compound of magnesium, chlorine and oxygen used as a drying agent is:
  - (a) magnesium oxychlorite, Mg(OCl)<sub>2</sub>
  - (b) magnesium chlorate, Mg(ClO<sub>3</sub>)<sub>2</sub>
  - (c) magnesium perchlorate, Mg(ClO<sub>4</sub>)<sub>2</sub>
  - (d) none of the above

[Hint: Magnesium perchlorate (anhydrone) has strong affinity for water giving Mg(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. It loses whole of water when heated at 250°C and drying property is regenerated.]

15. Match (X) with (Y) and select the correct alternative.

- 1. CaH<sub>2</sub>
- A. Sorel cement B. Anhydrone
- 2.  $BaSO_4 + ZnS$

Y

- C. Hydrolith
- 3. MgCl<sub>2</sub>·5MgO·xH<sub>2</sub>O
- D. Lithopone

X

- $Mg(ClO_4)_2$
- Α В C D
- 3 4 1
- 1 3 2 (c) 4
- (d) 4 1 2 3
- 16. Which are correct statements?
  - (a) Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is present in bones
  - (b)  $3Ca_3(PO_4)_2 \cdot CaF_2$  is part of enamel on teeth
  - (c) Ca<sup>2+</sup> ions are important in blood clotting
  - (d) Chlorophyll is a compound of calcium
- 17. Which are correct statements for Be and Al?
  - (a) Both have sp-hybridization-in their compounds.
  - (b) Both are rendered passive by concentrated HNO<sub>3</sub>.
  - (c) Both form amphoteric oxides.
  - (d) Both form ionic hydrides.
- 18. Chemical A is used for water softening to remove temporary hardness. A reacts with sodium carbonate to generate caustic soda. When CO<sub>2</sub> is bubbled through A, it turns cloudy. What is the chemical formula of A?
  - (a) CaCO<sub>3</sub>
- (b) CaO
- (c) Ca(OH)2
- (d)  $Ca(HCO_3)_2$

 $Ca(OH)_2 + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + 2H_2O$ Hint: Ca(OH)2 + Na2CO3 ---- CaCO3 + 2NaOH  $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$  ]

- Salt used as a purgative is:
  - (a) NaCl

- (b) MgSO<sub>4</sub>·7H<sub>2</sub>O
- (c) MgCl<sub>2</sub>·6H<sub>2</sub>O
- (d) Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>
- Water is added to calcium carbide and the evolved gas is passed through dilute H<sub>2</sub>SO<sub>4</sub> containing HgSO<sub>4</sub>. The organic compound formed is:
  - (a) HCHO
- (b) CH<sub>3</sub>CHO
- (c) CH<sub>3</sub>COOH
- (d) HCOOH

- 1. (d)
- 2. (a)
- 3. (b)
- 5. (b)
- **6.** (c)
- 7. (a)
- 8. (d)
- **9.** (b)
- **10.** (c)
- 12. (a)

- 13. (d)
- 14. (c)
- 15. (c)
- 4. (c) 16. (a, b, c)
- **17.** (b, c)

### Matrix Matching Questions for IIT Aspirants

Match List-I with List-II:

### List-I

#### List-II

- (a) Sorel's cement
- (p) MgCl<sub>2</sub>
- (b) Albite
- (q) MgO
- (c) A salt of carnallite
- (r) NaAlSi<sub>3</sub>O<sub>8</sub>
- (d) Glauber's salt
- (s) Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O
- Match the metals in List-I with their ore in List-II and formula in List-III:

List-I
--------

### List-II

### List-III

(Metal)

(Name of ore)

(Composition of ore)

- (a) Lithium (b) Sodium
- (p) Kiesserite (q) Spodumene
- (u) LiAlSi2O6 (v) NaNO<sub>3</sub>

- (c) Calcium
- (w) MgSO<sub>4</sub>·H<sub>2</sub>O

- (r) Fluorspar

- (d) Magnesium
- (s) Chile saltpetre
- (x) CaF<sub>2</sub>

(e-s)

- 3. Match the common name of the compounds in List-I with its chemical formula in List-II:

#### List-I

(a) Brine

- (b) Rock salt
- (q) NaCl
- (c) Sylvine
- (r)  $MgSO_4 \cdot 7H_2O$
- (d) Epsomite
- (e) Fly ash

- List-II
- (p) KCl
- (s) CaSiO<sub>3</sub>

Match the elements in List-I with their nature in List-II:

### List-I

- (a) Be
- (b) Fr
- (c) Ra
- (d) Mg
- Match List-I with List-II:

#### List-I

#### (Compounds)

- (a) Magnesium oxide
- (b) Barium sulphate
- (c) Calcium cyanamide
- (d) Magnesium sulphate

- List-II
- (p) Radioactive
- (q) Form covalent hydride
- (r) Form amphoteric oxide
- (s) Do not impart any colour
- to Bunsen flame

#### List-II

### (Use of compounds)

- (p) Fertilizer
- (q) Purgative
- (r) As a constituent of sorel cement
- (s) As a constituent of lithopone
- (t) Refractory material

(a-p, q)

3.

(a-q-u)

(a-q)

(b-s-v)

(b-q)

- (c-p) (c-r-x)(c-p)
- (d-s)(d-p-w)(d-r)

- (a-q, r, s) (b-p)
- (c-p)
- (d-s)(d-q)
- (a-r, t) (b-s)(c-p)

### Assertion-Reason Type Questions

In each of the following questions, two statements are given as Assertion (A) and Reason (R). Examine the statements and answer the questions according to the instructions given below. Mark:

- (a) if both (A) and (R) are correct and (R) is the correct explanation of (A).
- (b) if both (A) and (R) are correct and (R) is not the correct explanation of (A).
- (c) if (A) is correct and (R) is wrong.
- (d) if (A) is wrong and (R) is correct.
- (e) if both (A) and (R) are wrong.
- 1. (A) Beryllium and magnesium do not impart characteristic colour to the Bunsen-burner flame.
  - (R) Both Beryllium and magnesium have high ionisation energy.
- 2. (A) Be(OH)<sub>2</sub> dissolves in excess of NaOH.
  - (R) Be(OH)<sub>2</sub> is an amphoteric compound.
- 3. (A) Alkaline earth metals are softer than alkali metals.
  - (R) Atomic radii of alkaline earth metals are smaller than corresponding alkali metals in the same periods of periodic table.

- 4. (A) Beryllium compounds are covalent in nature.
  - (R) The size of Be<sup>2+</sup> ion is larger in comparison to the radii of the other divalent ions of alkaline earth metals.
- 5. (A) Lithium resembles magnesium.
  - (R) Li<sup>+</sup> has same size as Mg<sup>2+</sup>.
- [A.I.I.M.S. 1997]
- 6. (A) The fluorides of alkaline earth metals are almost insoluble in water.
  - (R) The lattice energies of the fluorides of alkaline earth metals are very high.
- 7. (A) Sulphur is estimated as BaSO<sub>4</sub> and not as MgSO<sub>4</sub>.
   (R) The ionic radius of Mg<sup>2+</sup> is smaller than that of Ba<sup>2+</sup>
- 8. (A) Na<sub>2</sub>SO<sub>4</sub> is soluble in water but BaSO<sub>4</sub> is insoluble.
  - (R) Lattice energy of barium sulphate exceeds its hydration [A.I.I.M.S. 1997]
- 9. (A) MgO is used for lining of steel making furnace.
  - (R) MgO is an acidic flux.
- 10. (A) Magnesium gets oxidised when heated in CO<sub>2</sub> or SO<sub>2</sub>
  - (R) Magnesium has a strong affinity for oxygen.

### tuswers

1. (a)

2. (b)

3. (d)

**4.** (c)

5. (a)

**6.** (a)

7. (b)

8. (a)

9. (c)

10. (a)

### HOUGH

### THOUGHT 1

Both alkaline earth metals and alkali metals are s-block elements. They resemble with each other in many respects but still there are certain dissimilarities in their properties on account of different number of electrons in the valency shell, smaller atomic radii, higher ionisation potential, higher electronegativity, etc.

Like lithium, beryllium also differs from rest of the alkaline earth metals on account of its small atomic size and high electronegativity. Be<sup>2+</sup> ion is very small and exerts a high polarising effect on any anion associated with it.

- 1. The correct sequence of increasing covalent character is represented by:

  - (a)  $BeCl_2 < NaCl < LiCl$  (b)  $NaCl < LiCl < BeCl_2$

  - (c) BeCl<sub>2</sub> < LiCl < NaCl (d) LiCl < NaCl < BeCl<sub>2</sub>
- 2. Which is least thermally stable?
  - (a) Li<sub>2</sub>CO<sub>3</sub>
- (b) MgCO<sub>3</sub>
- (c) BaCO<sub>3</sub>
- (d) BeCO<sub>3</sub>
- 3. Which of the following statements are true for II A group elements?
  - (a) Lattice energy of oxides, carbonates, fluorides decreases from Be to Ba.
  - (b) All form nitrides in air.
  - (c) The solubility of the hydroxides increases from Be to Ba.
  - (d) All are correct.
- The alkaline earth metal which does not directly combine with hydrogen is:
  - (a) Be

(b) Ca

(c) Sr

- (d) Ba
- 5. The solubility in water of sulphates down the IIA group is: Be > Mg > Ca > Sr > Ba

This is due to:

- (a) increase in melting point
- (b) increasing molecular mass
- (c) decreasing lattice energy
- (d) high heat of solvation for smaller ions
- 6. Which of the bicarbonate does not exist in solid state?
  - (a) NaHCO<sub>3</sub>
- (b) KHCO<sub>3</sub>
- (c) Ca(HCO<sub>3</sub>)<sub>2</sub>
- (d) RbHCO<sub>3</sub>

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- 7. The element which does not directly combine with carbon on strong heating:
  - (a) Li

(b) Be

(c) K

(d) Ca

### **THOUGHT 2**

Cement is one of the most important building material of the present time. It is a dirty greyish heavy powder containing cal-

cium aluminates and silicates. The important raw materials needed for the manufacture of cement are, limestone, clay and gypsum. The main step in the manufacture of cement is the heating of raw meal or slurry in the rotary kiln at a very high temperature 1400-1600°C. Finally 2 or 3% gypsum is added.

When cement is mixed with water and left as such for some time, it becomes a hard mass. This is known as setting of cement. It is believed that various aluminates and silicates present in the cement form hydrates with water which separate in the form of gel. The gels formed start losing water partly by evaporation and partly by forming hydrates with unhydrated constituents. This results in the formation of a hard mass.

- 1. Portland cement does not contain:
  - (a) CaSiO<sub>4</sub>
- (b) CaSiO<sub>3</sub>
- (c) Ca<sub>3</sub>·Al<sub>2</sub>O<sub>6</sub>
- (d) Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>
- 2. Setting of cement is:
  - (a) exothermic reaction
- (b) endothermic reaction
- (c) hydration process
- (d) none of these
- 3. The percentage of lime in portland cement is approximately:
  - (a) 20 25%
- (b) 30 40%
- (c) 60-65%
- (d) 40 50%
- 4. Concrete is a mixture of:
  - (a) cement, sand, gravel and water
  - (b) cement, limestone and water
  - (c) cement, slaked lime and water
  - (d) cement, sand and water
- 5. Gypsum is added to portland cement:
  - (a) to fasten the process of setting
  - (b) to slow down the process of setting
  - (c) to improve the colour of the cement
  - (d) all of the above are incorrect

### THOUGHT 3

Metal nitrate (A) on heating decomposes, leaving a solid residue (B) which goes into solution with dilute HCl. The solution of (B)gives a white precipitate with ammonium carbonate solution. The precipitate (C) is dissolved in dilute HCl and the solution is treated with potassium chromate to get yellow precipitate (D). The solution (B) with dilute H<sub>2</sub>SO<sub>4</sub> also gives a white precipitate (E) insoluble in dilute HCl and nitric acid. The precipitate (E) is a part of a white pigment lithopone.

- 1. The compound (E) is:
  - (a) BaSO<sub>4</sub>
- (b) MgSO<sub>4</sub>

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- (c) CaSO<sub>4</sub>
- (d) Na<sub>2</sub>SO<sub>4</sub>
- 2. The yellow precipitate (D) is:
  - (a) PbCrO<sub>4</sub>
- (b) BaCrO<sub>4</sub>
- (c) CaCrO<sub>4</sub>
- (d) none of these

3. The metal nitrate (A) is:

(a) Ca(NO<sub>3</sub>)<sub>2</sub>

(b)  $Pb(NO_3)_2$ 

(c) Ba(NO<sub>3</sub>)<sub>2</sub>

(d) KNO<sub>3</sub>

**4.** The solid residue (B) is:

(a) CaO

(b) PbO

(c) ZnO (d) BaO

5. The nitrate (A) can be confirmed by flame test. The colour

imparted by the salt to the flame is:

(a) yellow

(b) green

(c) blue

(d) red

### **THOUGHT 4**

Limestone is a naturally occuring form of calcium carbonate. It is used as building material and also for manufacture of other building materials such as Portland cement. It is used for the production of quick lime and slaked lime which have wide applications in chemical, metallurgical and construction industry. The pure CaCO3, ealled precipitated calcium carbonate, is used extensively as filler providing bulk to materials such as paint, plastics, printing inks and rubber. It is also used in toothpastes, cosmetics and antacids. Quick lime and slaked lime are the cheapest and most widely used bases for neutralising unwanted acids. Lime is used to neutralise acidic soils. An important application of quick lime is in air pollution control for the removal of SO2 in electric power plants. Slaked lime is used in the

manufacture of other alkalies and bleaching powder, in sugar refining, in tanning hides and in water softening.

1. The substance not likely to contain CaCO3 is:

(a) dolomite

(b) a marble statue

(c) sea shells

(d) calcined gypsum

2. Slaked lime reacts with chlorine to give:

(a) CaCl<sub>2</sub>

(b) CaO

(c) CaOCl<sub>2</sub>

(d) CaCO<sub>3</sub>

3. Quick lime is:

(a) CaO

(b) CaCO<sub>3</sub>

(c) Ca(OH)<sub>2</sub>

(d) CaSO<sub>4</sub>

4. The drying agent which absorbs CO<sub>2</sub> and reacts violently with water is:

(a) sodium carbonate

(b) quick lime

(c) conc. H<sub>2</sub>SO<sub>4</sub>

(d) alcohol

5. Chemical compound 'A' is used to remove temporary hardness from water. It reacts with Na<sub>2</sub>CO<sub>3</sub> to generate caustic soda. When CO<sub>2</sub> is passed through 'A' it turns cloudy. What is 'A'?

(a) CaCO<sub>3</sub>

(b) Ca(HCO<sub>3</sub>)<sub>2</sub>

(c) Ca(OH)<sub>2</sub>

(d) CaCl<sub>2</sub>

**6.** Quick lime is used in electric power plants with carbon to check pollution. What product of calcium is formed?

(a) CaSO<sub>3</sub>

(b) CaSO<sub>4</sub>

(c) CaS

(d) CaSO<sub>4</sub>·10H<sub>2</sub>O

### Answers

		and the second s					
Thought 1	<b>1.</b> (b)	<b>2.</b> (d)	<b>3.</b> (d)	<b>4.</b> (a)	<b>5.</b> (d)	<b>6.</b> (c)	<b>7.</b> (c)
Thought 2	1. (d)	<b>2.</b> (a, c)	3. (c)	<b>4.</b> (a)	<b>5.</b> (b)		
Thought 3	<b>1.</b> (a)	<b>2.</b> (b)	<b>3.</b> (c)	<b>4.</b> (d)	<b>5.</b> (b)		
Thought 4	<b>1.</b> (d)	<b>2.</b> (c)	/ 3, (a)	<b>4.</b> (b)	5. (c)	6. (a)	

### INTEGER ANSWER Type Questions

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. How many alkaline earth metals are known?
- 2. How many water molecules are associated with 'Epsom salt'?
- 3. Magnesium oxide when mixed with a saturated solution of magnesium chloride sets to a hard mass like cement known as 'sorel cement'. The composition of sorel cement is MgCl<sub>2</sub>nMgOxH<sub>2</sub>O. What is the value of n?
- 4. On heating calcium ammoniate, ammonia and hydrogen are evolved. How many moles of ammonia are evolved when 1.5 moles of calcium ammoniate are heated?
- 5. Magnalium is an alloy of aluminium and magnesium. What is the percentage of magnesium in this alloy?
- 6. Calcium carbide reacts with nitrogen and forms an important fertilizer, calcium cyanamide. How much calcium cyanamide is formed when 3.2 g of calcium carbide is completely converted into cyanamide?

### Answers

- 1. (6) Be, Mg, Ca, Sr, Ba and Ra are alkaline earth metals.
- 2. (7) Epsom salt has the molecular formula, MgSO<sub>4</sub>·7H<sub>2</sub>O.
- 3. (5)  $MgCl_2 \cdot 5MgOxH_2O$
- 4. (8)  $3\text{Ca}(\text{NH}_3)_6 \longrightarrow \text{Ca}_3\text{N}_2 + 16\text{NH}_3 + 3\text{H}_2$  $\begin{array}{c} 3 \text{ moles} \\ 1.5 \text{ moles} \\ \end{array}$  8 moles

- 5. (5) Magnalium: 95% Al + 5% Mg
- 6. (4)  $CaC_2 + N_2 \longrightarrow CaCN_2 + C$ 64 g
  80 g

$$=\frac{80}{64}\times3.2=4$$

## Revision Exercise (Chapter 5 to 7)



NIC	GLE CORRECT ANSWER TYPE			(d) all of these	Ш
1.	The pair that yields the same gaseous product on reacti	on	10.	The deep colour produced when iodine is dissolved in solution of KI is caused by the presence of:	a a
	with water:			(a) $I_3$ $\Box$ (b) $I^-$	
	(a) K and $KO_2$ $\square$ (b) Ca and $CaH_2$			$\begin{array}{ccc} \text{(a)} & I_3 & & \square & \text{(b)} & I \\ \text{(c)} & I_{\overline{2}} & & \square & \text{(d)} & I_2 \end{array}$	
	(c) Na and Na <sub>2</sub> O <sub>2</sub> $\Box$ (d) Ba and BaO <sub>2</sub>		11	Dissolving NaNH <sub>2</sub> in water will give:	<b></b>
2.	Acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> on oxidation by H <sub>2</sub> O <sub>2</sub> gives :		11.	(a) a solution containing solvated Na <sup>+</sup> ions, OH <sup>-</sup> ions a	and
	(a) Blue solution $\Box$ (b) $CrO_5$			NH <sub>3</sub>	anu —
	(c) Chromium peroxide $\Box$ (d) all of these			(b) a solution containing solvated Na <sup>+</sup> and NH <sub>2</sub> ions	
3.	Select the reaction which does not occur.			(c) NH <sub>3</sub> and metallic sodium	
	(a) $NaNH_2 + C \xrightarrow{750^{\circ}C} NaH + HCN$			(d) solvated Na <sup>+</sup> ions and hydrogen gas	
- 15 5000	(b) $6\text{NaOH} + 4\text{S} \xrightarrow{\text{Heat}} \text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{S} + 3\text{H}_2\text{O}$		12.	Temporary and permanent hardness can be removed	by
	(c) $Na(NH_4)HPO_4 \xrightarrow{Heat} NaPO_3 + NH_3 + H_2O$			addition of and respectively.	
				(a) $CaO, CaCO_3$ $\Box$ (b) $CaO, Na_2CO_3$	
4	(d) $2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$			(c) $Na_2CO_3$ , $CaO$ $\Box$ (d) $NaHCO_3$ , $CaCl_2$	
4.	The order of increasing thermal stabilities of		13.	$CO_2$ gas along with solid $(Y)$ is obtained when sodium s	
	$K_2CO_3$ , $MgCO_3$ , $CaCO_3$ , $BaCO_3$ is:			$(X)$ is heated. $(X)$ is again obtained when $CO_2$ gas is pass	sed
	$(I) \qquad (II) \qquad (IV)$			into aqueous solution $(Y)$ . $(X)$ and $(Y)$ are:	
	(a) $IV < II < III$			(a) $Na_2CO_3$ , $Na_2O$ $\square$ (b) $Na_2CO_3$ , $NaOH$	
	(c) $II < III < IV < I$ $\Box$ (d) $II < IV < III < I$			(c) $NaHCO_3$ , $Na_2CO_3$ $\square$ (d) $Na_2CO_3$ , $NaHCO_3$	
5.	Alkali metals form hydrated compounds. The hydrati	ion	14.	A metal $M$ readily forms water soluble $MSO_4$ . It also for	
	enthalpies of alkali metals are in the sequence of:			oxide MO which becomes inert on heating. Hydroxide M(Ol	-
	(a) $Rb^+ > Li^+ > Na^+ > K^+ > CS^+$			is insoluble in water but soluble in NaOH solution. Wha	ıt is
	(b) $CS^+ > Rb^+ > K^+ > Na^+ > Li^+$			M?	
	(c) $Li^+ > Na^+ > K^+ > Rb^+ > CS^+$			(a) Mg	
	(d) $K^+ > Na^+ > Li^+ > Rb^+ > CS^+$			(c) Ca	
6	The strength of 10 volume solution of hydrogen peroxide		15.	The correct order of equivalent conductivity at infin	nite
o.	(a) $22.79 \text{ g/L}$ $\Box$ (b) $30.36 \text{ g/L}$	□ □		dilution of LiCl, NaCl and KCl is:	
	(c) $18.5 \text{ g/L}$			(a) LiCl>NaCl>KCl	
7	Ozone reacts with $H_2O_2$ to give oxygen. One volume of ozone			(c) NaCl>KCl>LiCl	
- ' -	gives:	,,,,,	16.	Strong reductant in IIA and IA group is:	
	(a) one volume of oxygen			(a) Ba, Li	
	(b) half volume of oxygen		1	(c) Ba, Cs	
	(c) 1.5 volume of oxygen		17.	The compound (A) on heating gives a colourless gas.	
	(d) two volumes of oxygen			residue is dissolved in water to obtain (B). Excess of CO	
8	Which of the following is incorrect?	lal		bubbled through aqueous solution of $(B)$ , $(C)$ is formed.	
0.	(a) Hydrogen > Deuterium > Tritium (% relative abundan	ce)		on gentle heating gives back (A). The compound (A) is	
	(a) Hydrogon's Souterrain's Hillann' (N 101an', C abdillann			(a) $CaCO_3$ $\Box$ (b) $Na_2CO_3$	
	(b) Hydrogen > Deuterium > Tritium (melting point)		10	(c) $K_2CO_3$ $\Box$ (d) $CaSO_4 \cdot 2H_2O$	
	(c) Hydrogen < Deuterium < Tritium (boiling point)		18.	An alkaline earth metal (M) gives an insoluble sulphate.	
	(d) Hydrogen < Deuterium < Tritium (dissociation energ			mixture of the sulphate and a sulphide of 3d-block m	
	(a) Try drogon ( Dediction ( Triddin (dissociation energy			forms a white pigment which is known as <b>lithophone</b> . M	etai
9.	Highly pure dilute solution of sodium in liquid ammonia			(M) is:	
	(a) shows blue colour			(a) Ca □ (b) Mg (c) Ba □ (d) Sr	
	(b) exhibits electrical conductivity		10		
	(c) acts as a reducing agent		19.	The electrical conductivity of sodium dissolved in liquid N	NII3
	· / · · · · · · · · · · · · · · · · · ·			is due to:	

	(a) ammoniated Na ions Li (b) ammoniated electrons i	U <u>(</u>	<u> IVIC</u>	E OR MORE THAN ONE CORRECT	
	(c) both (a) and (b) $\square$ (d) none of these		ANS	SWERS TYPE	
20.	Which of the following compounds is known as pearl ask	1?	21	Identify the compat statements	
	(a) $KMnO_4$		31.	Identify the correct statements:	
				(a) Mass of H-atom is $1.66 \times 10^{-27}$ kg.	
	Slaked lime is obtained when water is added to:			(b) Cu dissolves in H <sub>2</sub> SO <sub>4</sub> and liberates H <sub>2</sub> .	
	1			(c) H <sub>2</sub> is liberated by the action of Al with conc. NaOH	
		_		(d) Hydrogen contains at room temperature 25% para	and
	Which of the following is generally used for clearing sno			75% ortho form.	
<i>LL</i> .		W	32.	Identify the incorrect statements:	
	from roads during winters in cold countries?  (a) CaF <sub>2</sub>	_		(a) The reactivity of hydrogen towards halogens is in	the
				order $Cl_2 > Br_2 > I_2 > F_2$ .	
22				(b) The oxides of hydrogen and deuterium are neutral.	
25.	The hydride gap refers to inability of:			(c) Molecular hydrogen reduces ZnO and CuO to Zn	and
	(m) 110 110 Busin 10 10 110 110 110 110 110 110 110 110			Cu respectively.	
	(b) elements of group 7, 8 and 9 of the <i>d</i> -block to for			(d) Atomic hydrogen reduces KMnO <sub>4</sub> to meta	allic
				manganese.	
			33.	When chlorine is passed through NaOH solution un	nder
	(d) s-electrons of valency shell of p-block elements to par	ti- 		different dilutions, the main products formed are:	
•	cipate in bonding	⊔		(a) NaCl, NaClO $\Box$ (b) NaCl, NaClO <sub>2</sub>	
24.	Hydride of certain non-metallic element 'X' is amphoteric			(c) NaCl, NaClO <sub>3</sub> $\square$ (d) NaCl, NaClO <sub>4</sub>	
	nature. The hydride of 'X' also reacts with calcium hydrid		34.	Which of the following metals do react with nitrogen w	hen
	(hydrolith) to liberate dihydrogen gas. The element 'X' is	_		heated in its atmosphere?	
				(a) Ca	
	- (-)			(c) Li	
25.	In which of the following reactions water does not act	as	35.	Which of the following nitrates give NO <sub>2</sub> on heating?	
	hydrolytic agent?			(a) $NaNO_3$	
				(c) $KNO_3$	
	() -3-22		36.	Which of the following statements about alkaline earth me	etals
26.	Which elements out of the following do not produ	ce		are correct?	
	hydrogen on treatment with caustic soda?			(a) Hydration energy of Sr <sup>2+</sup> is greater than that of Be <sup>2</sup>	!+.□
	(1) Zn (2) Sn (3) Mg (4) Cu (5) Al	_		(b) CaCO <sub>3</sub> decomposes at a higher temperature than BaC	$CO_3$ .
	(a) (1) and (5)				
	(c) (4) and (5)			(c) Ba(OH) <sub>2</sub> is stronger base than Mg(OH) <sub>2</sub> .	
27.	Which of the following hydrides does conduct electricity	y? 		(d) SrSO <sub>4</sub> is less soluble in water than CaSO <sub>4</sub> .	
	(a) $GeH_2$ $\Box$ (b) $SiH_4$		37.	In which of the following alloys Mg is present?	
••	(c) $B_2H_6$ $\Box$ (d) NaH			(a) Electron	
28.	Sodium oxide cannot be obtained by heating which of t	he		(b) Magnalium	
	following?			(c) Duraluminium	
	(a) NaOCl			(d) Aluminium bronze	
•	* * * * * * * * * * * * * * * * * * * *		38.	KO <sub>2</sub> finds use in oxygen cylinders used for space	and
29.	Portland cement contains the following amount of CaO:			submarines. The fact(s) related to such use of KO2 is/as	re:
	(a) 70-80%			(a) it produces O <sub>2</sub>	
•	(c) 50-60%			(b) it produces O <sub>3</sub>	
30.	•			(c) it absorbs CO <sub>2</sub>	
	(a) electrolysis of fused MgCl <sub>2</sub>			(d) it absorbs N <sub>2</sub> and CO <sub>2</sub> both	
	(b) reduction of MgCl <sub>2</sub> with carbon		39.	In comparison to alkaline earth metals, alkali metals are	:
	(c) electrolysis of aqueous solution of MgCl <sub>2</sub>			(a) more reactive $\square$ (b) less reducing	
	(d) roasting of MgCO <sub>3</sub>			(c) more soft	

40.	Select the wrong statement:	
	(a) The formula of plaster of paris is CaSO <sub>4</sub> ·2H <sub>2</sub> O.	
	(b) MgCO <sub>3</sub> is commonly used in making toothpaste.	
	(c) BeO is a basic oxide.	
	(d) Calcium fluoride is insoluble in water.	

### ASSERTION-REASON TYPE QUESTIONS

Each of the following questions contains statements of **Assertion** (A) and **Reason** (R). Mark the correct answer according to the following code:

- (a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
- (c) If (A) is correct but (R) is incorrect.
- (d) If both (A) and (R) are not correct.
- 41. (A) Hydrogen peroxide in the form of aqueous solution acts as a bleaching agent of delicate materials such as wool, silk, cotton, hair, etc.
  - (R)  $H_2O_2$  acts as a bleaching agent due to its oxidising nature. Coloured material + [O]  $\longrightarrow$  Colourless
- **42.** (A) Normal hydrogen is a mixture of two forms : ortho 75% and para 25%.
  - (R) Pure para-form can be obtained at low temperature but pure ortho-form cannot be obtained.
- **43.** (A) Lithium when heated in the atmosphere of nitrogen forms lithium nitride while other alkali metals do not combine with nitrogen.
  - (R) Lithium is the most reactive alkali metal as its ionisation potential is lowest amongst alkali metals.
- 44. (A) K<sub>2</sub>CO<sub>3</sub> like Na<sub>2</sub>CO<sub>3</sub> can be prepared by Solvay's process.
  - (R) K<sub>2</sub>CO<sub>3</sub> on heating decomposes giving carbon dioxide.
- 45. (A) Alkaline earth metals are harder than alkali metals.
  - (R) The metallic bonding is higher in alkaline earth metals as these possess two electrons in the valence shell.
- **46.** (A) Chemical reduction methods are not applicable for the extraction of alkali and alkaline earth metals.
  - (R) Alkali and alkaline earth metals are themselves strong reducing agents.
- 47. (A) Magnesium and beryllium do not impart colour to flame.
  - (R) Both have high ionisation energies.
- 48. (A) Li<sup>+</sup> has low mobility in aqueous solution.
  - (R) Lithium ion has low tendency of hydration as its size is small.
- **49.** (A)  $H_2O_2$  is a neutral compound.
  - (R)  $H_2O_2$  is an ionic compound.
- **50.** (A) Superoxides are formed by K, Rb and Cs.
  - (R) Superoxides are paramagnetic and coloured.

### **MATRIX MATCHING QUESTIONS**

51. Match Column-I with Column-II:

#### 

52. Match Column-I with Column-II:

# Column-I (a) Sodium (b) Sodium carbonate (c) Potassium (d) Caesium (d) Caesium (e) Potassium (f) Photoelectric cell (g) Nuclear reactor (g) Special thermometers to measure high temperature

**53.** Match Column-I with Column-II:

Column-I	Column-II
(a) NaCl	(p) Sylvine
(b) KCl	(q) Brine
(c) MgCl <sub>2</sub>	(r) Sorel's cement
(d) $CaCN_2 + C$	(s) Rock salt
	(t) Fertilizer

### LINKED COMPREHENSION TYPE

### Passage 1

Lithium and beryllium, the first members of alkali metals and alkaline earth metals respectively, show anomalous behaviour *i.e.*, differ from the rest of the members of their family. The main reasons for their difference are:

- (i) exceptionally small atomic and ionic size
- (ii) high ionisation energy
- (iii) absence of d-orbitals in their valence shell
- (iv) high polarising power of the cations

Answer the following questions:

- 54. Which of the following has the lowest melting point?
  - (a) LiCl (b) NaCl (c) KCl (d) RbCl
- 55. Mg and Li are similar in their properties due to:
  - (a) same e/m ratio
- (b) same electron affinity
- (c) same group
- (d) same ionic potential
- **56.** Which of the following alkali metal ions has the minimum ionic mobility in aqueous solution?
  - (a) Na<sup>+</sup>

(b) K<sup>+</sup>

(c) Li<sup>+</sup>

(d) Cs+

**57.** Be(OH)<sub>2</sub> is:

(a) acidic

(b) basic

(c) amphoteric

(d) neutral

58. Which is least thermally stable?

(a) Li<sub>2</sub>CO<sub>3</sub>

(b) MgCO<sub>3</sub>

(c) BaCO<sub>3</sub>

(d) BeCO<sub>3</sub>

### Passage 2

Hydrogen gas has been considered as one of the alternate sources of energy. The advantage of using hydrogen as a fuel is that it is environmentally clean. The second advantage with hydrogen is that the heat of combustion of hydrogen per gram is higher than any other fuel. But, there are many problems in storing and transportation of hydrogen gas.

Answer the following questions:

59. Which fuel does produce least environmental pollution?

(a) Gasoline

(b) Hydrogen

(c) Wood

(d) Coal

60. Liquid H2 has been used as a rocket fuel because of:

(a) high thrust

(b) small space it occupies

(c) its reaction with oxygen is highly exothermic

(d) all the above are correct

61. Which methods can be used to store hydrogen?

(a) By absorbing hydrogen on activated carbon

(b) Reacting hydrogen with lithium to form LiH

(c) The alloy, LaNi<sub>5</sub>, has high capacity to take up hydrogen

(d) All of the above

### Passage 3

The solubility of an ionic compound in water mainly depends on two factors.

(i) Lattice energy and (ii) hydration energy

Both these factors oppose each other and the resultant of these guides the solubility of the compound in water. If lattice energy has greater value, the solubility is less. In case, hydration energy is more, then the compound is freely soluble in water.

Answer the following questions:

**62.** Compounds of alkaline earth metals are less soluble in water in comparison to alkali metals. This is due to:

(a) their higher ionisation energies

(b) their high lattice energies

(c) their high hydration energies

(d) their increased covalent nature

63. Which of the following is most soluble in water?

(a) MgSO<sub>4</sub>

(b) CaSO<sub>4</sub>

(c) SrSO<sub>4</sub>

(d) BaSO<sub>4</sub>

**64.** BeF<sub>2</sub> is soluble in water whereas fluorides of other alkaline earth metals are insoluble because of :

(a) ionic nature of BeF<sub>2</sub>

(b) covalent nature of BeF2

(c) greater hydration energy of Be<sup>2+</sup> ion

(d) greater lattice enrgy of Be<sup>2+</sup> ion

### **INTEGER ANSWER TYPE**

65. How many alkali metals are known?

66. How many neutrons are present in tritium atom?

67. How many isotopes of hydrogen are known?

**68.** In water, each H<sub>2</sub>O molecule is surrounded by ...... neighbouring H<sub>2</sub>O molecules randomly by hydrogen bonding.

69. What is the degree of hardness of a sample of water containing 10.8 mg of MgSO<sub>4</sub> (Mol. mass 120) per kg of water?

**70.** Of all the alkali metals, only sodium and potassium are found in abundance in nature *i.e.*, they are ....th and ....th most abundant elements by weight in earth's crust.

**71.** How many water molecules are present as water of crystallisation in the molecule of gypsum?

### Answers with Hints

(b) Both Ca and CaH<sub>2</sub> on reaction with water evolve hydrogen gas.
 Ca + 2H<sub>2</sub>O → Ca(OH)<sub>2</sub> + H<sub>2</sub>
 CaH<sub>2</sub> + 2H<sub>2</sub>O → Ca(OH)<sub>2</sub> + 2H<sub>2</sub>

**2.** (d)

 $K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow 2CrO_5 + K_2SO_4 + 5H_2O$ Chromium
peroxide(blue)

3. (a)  $NaNH_2 + C \xrightarrow{Heat} NaCN + H_2 \uparrow$ 

 $\begin{array}{lll} \textbf{4.} & \text{(c)} & \text{Alkali metals carbonates except } \text{Li}_2\text{CO}_3 \text{ do not decompose on} \\ & \text{heating. The thermal stability of alkaline earth metals carbonates} \\ & \text{increases from top to bottom.} \end{array}$ 

5. (c) Smaller the ion, higher is degree of hydration *i.e.*, high is hydration enthalpy. Thus, the hydration enthalpies decrease as the size of ion increases from Li<sup>+</sup> to Cs<sup>+</sup>.

**6.** (b) % strength =  $\frac{17}{56}$  × volume strength =  $\frac{17}{56}$  × 10 = 3.036 *i.e.*, 30.36 g/L

7. (d)  $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$ 1 vol 2 vol

8. (b) Hydrogen < Deuterium < Tritium  $_{20.60 \text{ K}}$  (melting point)

**9.** (d)

- 10. (a) KI +  $I_2 \longrightarrow KI_3 (I_3^-)$
- 11. (a)  $NaNH_2 + H_2O \longrightarrow Na^+(aq.) + OH^- + NH_3$
- 12. (b)  $M(HCO_3)_2 + CaO \longrightarrow \underbrace{MCO_3 + CaCO_3}_{Insoluble} + H_2O$

$$MCl_2 + Na_2CO_3 \longrightarrow MCO_3 + 2NaCl$$
Insoluble Soluble

$$MSO_4 + Na_2CO_3 \longrightarrow MCO_3 + Na_2SO_4$$
Insoluble Soluble

13. (c) 
$$2\text{NaHCO}_3 \longrightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}_2$$
(Y) (Y)

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$
(X)
(Y)

14. (d) BeSO<sub>4</sub> is soluble in water. BeO becomes inert on heating. Be(OH)<sub>2</sub> is insoluble and reacts with NaOH. The product is soluble in water.

$$Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$
Soluble

- 15. (b) Ionic mobility depends on the size of ion. The ionic size in case of hydrated cation is  $K_{aq}^+ < Na_{aq}^+ < Li_{aq}^+$ .
- 16. (a) The maximum value of oxidation potential of lithium makes it strongest reducing agent amongst alkali metals.
  The values of oxidation potentials increase from top to bottom in IIA group. Thus, Ba is a strong oxidising agent.

17. (a) 
$$CaCO_3 \longrightarrow CaO + CO_2$$

$$\downarrow H_2O \qquad \qquad Calcurless$$

$$CO_2 \longrightarrow Ca(OH)_2 \longrightarrow Ca(HCO_3)_2 \xrightarrow{Heat} CaCO_3$$

$$(B) \qquad (C) \qquad (A)$$

- 18. (c) (BaSO<sub>4</sub> + ZnS) is a white pigment known as lithophone.
- **19.** (c) Na + (x + y) NH<sub>3</sub>  $\longrightarrow$  Na<sup>+</sup>(NH<sub>3</sub>)<sub>x</sub> +  $e^{-1}$ (NH<sub>3</sub>)<sub>y</sub>
- 20. (b)
- 21. (d)  $CaO + H_2O \longrightarrow Ca(OH)_2$
- 22. (d) 23. (b)
- 24. (c) 'X' is oxygen.  $H_2O$  is amphoteric.  $CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$
- 25. (d) Water acts as a proton donor when it reacts with NH<sub>3</sub>.
- **26.** (b)
- 27. (d) NaH is an ionic hydride. In molten state, it conducts electricity.

28. (d) 
$$2\text{NaOCl} \longrightarrow 2\text{NaCl} + \text{O}_2$$
  
 $2\text{NaHCO}_3 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$   
 $2\text{NaNO}_3 \longrightarrow 2\text{NaNO}_2 + \text{O}_2$ 

- 29. (c) 30. (a)
- **31.** (a, c, d)
- 32. (a, d) The reactivity of hydrogen towards halogens is in the order  $F_2 > Cl_2 > Br_2 > I_2$ . Atomic hydrogen reduces acidified KMnO<sub>4</sub> to manganous salt.

33. (a, c) 
$$Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O$$

$$3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

34. (a, b, c) 
$$3Ca + N_2 \longrightarrow Ca_3N_2$$
$$3Mg + N_2 \longrightarrow Mg_3N_2$$
$$6Li + N_2 \longrightarrow 2Li_3N$$

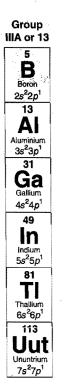
35. (b, d) 
$$Ba(NO_3)_2 \longrightarrow BaO + 2NO_2 + \frac{1}{2}O_2$$
$$2LiNO_3 \longrightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$$

- 36. (c, d) 37. (a, b, c) 38. (a, c) 39. (a, c, d)
- 40. (a, c) The formula of plaster of paris is CaSO<sub>4</sub>· ½ H<sub>2</sub>O<sub>4</sub>.
  BeO is an amphoteric oxide.
- 41. (a) 42. (b) 43. (c) 44. (d) 45. (a) 46. (a) 47. (a)
- **48.** (c) **49.** (d) **50.** (b)
- **51.** (a-p, r); (b-p); (c-q, t); (d-q, s)
- **52.** (a-p, s, t); (b-p, q); (c-r, t); (d-r)
- **53.** (a-q, s); (b-p, t); (c-r); (d-t)
- **54.** (a) Due to high polarising power of Li<sup>+</sup> ion, LiCl shows somewhat covalent nature.
- 55. (d)
- **56.** (c) Li<sup>+</sup> ion being smallest in size has high degree of hydration.
- 57. (c) Be(OH)<sub>2</sub> combines both with acid and alkali.
- 58. (d) 59. (b) 60. (d) 61. (d)
- **62.** (b) The cations have small ionic size and double the charge in comparison to alkali metal ions. Therefore, their lattice energies are high.
- **63.** (a) **64.** (c) **65.** (6) **66.** (2) **67.** (3) **68.** (4)
- 69. (9) 10.8 mg of MgSO<sub>4</sub> is present in 10<sup>3</sup> g of water.

Thus, 
$$10^6$$
 g of water contains = 10800 mg of MgSO<sub>4</sub>  
= 10.8 g of MgSO<sub>4</sub>  
 $120$  g MgSO<sub>4</sub> =  $100$  g of CaCO<sub>3</sub>

So, 
$$10.8 \text{ g of MgSO}_4 = \frac{100 \text{ g of CaCO}_3}{120} \times 10.8 = 9 \text{ g CaCO}_3$$
  
Hardness of water = 9 ppm

- **70.** (7 and 8)
- **71.** (2)



# CHAPTER 8



### **Elements of Group IIIA or 13**

The Boron Family (ns<sup>2</sup>np<sup>1</sup>)

(Boron and Aluminium)

### Contents:

- **8.1** General Characteristics of Group IIIA or 13 Elements
- 8,2 Abnormal Behaviour of Boron
- 8.3 Comparison of Boron and Aluminium
- 8.4 Diagonal Relationship of Boron and Silicon
- 8.5 Boron
- 8.6 Compounds of Boron
- 8.7 Aluminium
- 8.8 Compounds of Aluminium
- 8.9 Goldschmidt's Alumino-Thermic Process

Group Period	ША 13	IVA 14
2	B (5)	C (6)
3	Al (13)	Si (14)
. 4	Ga (31)	Ge (32)
.5	In (49)	Sn (50)
6	T1 (81)	Pb (82)
7	Uut (113)	Uuq (114)

### 8.1 GENERAL CHARACTERISTICS OF GROUP IIIA OR 13 ELEMENTS

Group IIIA or 13 of the long form of the periodic table consists of six elements—boron, aluminium, gallium, indium, thallium and ununtrium. These are p-block elements as the last differentiating electron enters np orbital. The configuration of the outermost energy shell is  $ns^2$   $np^1$ , i.e., this group marks the beginning of the p-block elements. Since the members of this group possess three electrons in the outermost or in their valency shell, they have many similarities in their properties. However, the penultimate shell (next to the outermost) contains  $s^2$ -grouping in boron,  $s^2p^6$  (8 electrons) in aluminium and  $s^2p^6d^{10}$  (18 electrons) in other elements (Ga, In, Tl and Uut). This shows why boron differs from aluminium and both boron and aluminium having noble gas kernel differ from other four elements. The **electronic configuration** of these elements is given below:

Element	At. No.		Electronic configuration	Inert gas core
В	5	2, 3	$1s^2$ , $2s^2 2p^1$	[He] $2s^2 2p^1$
A1	13	2, 8, 3	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^1$	[Ne] $3s^2 3p^1$
Ga	31	2, 8, 18, 3	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^1$	[Ar] $3d^{10}$ , $4s^2 4p^1$
In	49	2, 8, 18, 18, 3	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ , $5s^2$ $5p^4$	[Kr] $4d^{10}$ , $5s^2$ $5p^1$
<b>T</b> 1	81	2, 8, 18, 32, 18, 3	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ , $5s^2$ $5p^6$ $5d^{10}$ , $6s^2$ $6p^1$	[Xe] $4f^{14}$ , $5d^{10}$ , $6s^2$ $6p$
Uut	113	2, 8, 18, 32, 32, 18, 3	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ , $5s^2$ $5p^6$ $5d^{10}$ $5f^{14}$ ,	[Rn] $5f^{14}$ , $6d^{10}$ , $7s^2$ $7p$
			$6s^2 6p^6 6d^{10}, 7s^2 7p^1$	

The members of this group are less metallic in comparison to elements of IA (alkali metals) and IIA (alkaline earth metals) groups. Boron is regarded as a semi-metal. It is closer to non-metals than metals in its properties. Aluminium and rest of the elements are metallic in nature. General characteristics of these elements\* are discussed below:

- 1. Abundance and occurrence: Aluminium is the most abundant metal and third most abundant element (after oxygen and silicon) by mass in the earth's crust. The most important ore of aluminium is bauxite. Boron is fairly rare element but it is well known because it occurs as concentrated deposits of borax, kernite and tourmaline crystal. Gallium is twice as abundant as boron, but indium and thallium are much less common. All the three elements (Ga, In and Tl) occur as sulphides in traces in zinc and lead sulphide ores.
- **2. Atomic and ionic radius:** The atomic radius increases from boron to thallium. Ionic radius  $(M^{3+})$  also increases.

However, gallium has an abnormal value of atomic radius, which is lower than that of aluminium.

	В	Al	Ga	In	Tl
Atomic radius (pm)	85	143	135	167	170
(Metallic)					
Ionic radius $M^{3+}$ (pm)	27	53.5	62	80.0	88.5

[There is no evidence for the existence of B<sup>3+</sup> and the value of ionic radius is an estimate.]

The sharp increase of atomic radius of Al is due to greater screening effect in aluminium due to the presence of eight electrons in the penultimate shell than in boron which has two electrons in the penultimate shell. Thus, outermost electrons in boron experience greater nuclear attraction than in aluminium resulting thereby smaller atomic radii in boron in comparison to aluminium.

Ga, In and Tl follow after a row of ten transition elements. Thus, there are ten d electrons in the penultimate shell which are less efficient in shielding the nuclear charge and outer electrons are firmly held by nucleus. Thus, atoms with a  $d^{10}$  inner shell are smaller than would otherwise be expected.

The large difference in size between B and Al results in many differences in properties.

The smaller value of gallium in comparison to aluminium is due to the fact that in going from Al to Ga the penultimate d-orbitals are filled in the first d-block series from Sc(21) to Zn (30). The d-electrons do not screen the nuclear charge in an effective manner and therefore, the electrons in the outermost shell of gallium experience more force of attraction towards nucleus than aluminium, causing thereby decrease in atomic radius.

The atomic and ionic radii of group 13 elements are smaller than the corresponding elements of group 1 and 2 in the same period.

This is due to the fact that effective nuclear charge increases and electrons are pulled inwards resulting in a decrease in atomic size.

In isoelectronic species, the ionic size decreases with increase in atomic number, *i.e.*, *z/e* ratio.

$$Na^{+}$$
 >  $Mg^{2+}$  >  $Al^{3+}$  (102 pm) (72 pm) (53.5 pm)

**3. Density:** Density increases from boron to thallium. However, boron and aluminium have comparatively low values. This is due to their lower atomic masses as compared to gallium, indium and thallium.

**4. Melting and boiling points:** The elements of this group do not show a regular change in their melting points with increase in atomic number. The melting point decreases from B to Ga and then increases.

The high melting point of boron is due to the fact that it exists as a giant covalent polymer in both solid and liquid state. The elements Al, In and Tl all have close-packed metal structures. Gallium has an unusual structure. It consists of only Ga<sub>2</sub> molecules. It has, thus, low melting point. It exists as liquid up to 2000°C and hence used in high temperature thermometry.

However, the boiling points of the elements of IIIA group follow a regular decrease from boron to thallium. This shows that the strength of the bonds holding the atoms in liquid state decreases from boron to thallium.

- **5. Ionisation energy or ionisation enthalpies :** The following trends are observed:
- (i) The first ionisation energies of group 13 elements are lower than the corresponding elements of group 2, *i.e.*, alkaline earth metals in the same period. However, second ionisation energies of group 13 elements are higher in comparison to corresponding alkaline earth metals.
- (ii) On moving down the group from boron to thallium, a regular decreasing trend (expected) in the ionisation energy values is not observed. The ionisation energy decreases from B to Al, increases in Ga and again decreases in In. The value of ionisation energy of Tl is higher than In.
- (iii) The second and third ionisation energies for the elements are successively higher.

<sup>\*</sup>Thallium, is known as **Duckbill platypus** as it shows similarities with many other elements. Ununtrium, the last member of this group, is a synthetic and radioactive element. Very little is known about its characteristics.

The values o	f first, s	econd	and 1	third	ionisation	energy
of group 13 ele	ments a	are tab	ulate	d bel	ow:	

Til		Ionisati	on energy (l	kJ mol <sup>-1</sup> )
Element	1st	2nd	3rd	Sum of three
В	801	2427	3659	6887
. Al	577	1816	2744	5137
Ga	579	1979	2962	5520
Ĭn	558	1820	2704	5082
T1	589	1971	2877	5437

The elements of group 13 have  $ns^2np^1$ -grouping in the outermost energy shell. For the first ionisation energy, the electron has to be removed from the p-orbital in case of group 13 elements while in alkaline earth metals  $(ns^2)$ , the s-electron of the same energy shell has to be removed. Since, s-electron is nearer to nucleus in comparison to p-electron, it is more firmly held than p-electron due to strong attractive force. Hence, the removal of p-electron is easier and, therefore, the first ionisation energy values of group 13 elements are lower than the corresponding alkaline earth metals.

After the removal of p-electron, the elements of group 13 acquire  $ns^2$ -configuration while alkaline earth metals acquire  $ns^1$ -configuration. It is easier to remove electrons from  $ns^1$  in comparison to  $ns^2$  in the same energy shell. Hence, the second ionisation energy values of group 13 elements are higher than the corresponding alkaline earth metals.

The first ionisation energy of boron is highest in the group since, its size is smallest and screening effect is lowest. The sharp decrease from B to Al is due to appreciable increase in atomic size and the screening effect of s and p-electrons of the penultimate energy shell. In case of Ga, there are ten d-electrons in the penultimate energy shell which screen the nuclear charge less effectively and, thus, the outer electron is held firmly by the nucleus. As a result, the ionisation energy remains nearly the same as that of aluminium. In case of In, the number of d-electrons and their shielding effect remain the same as in gallium. The ionisation energy, however, decreases in indium due to increase in atomic size from Ga to In. The increase in ionisation energy from In to Tl is due to poor screening effect of 14f-electrons present in the inner energy shell.

After the loss of first electron, the effective nuclear charge increases with the result that decrease in ionic size occurs and thus, more and more energies are required for the removal of second, third and subsequent electrons.

$$IE_{\rm I} < IE_{\rm II} < IE_{\rm III} < IE_{\rm IV}$$

Since, the sum of first, second and third successive ionisation energies of the elements of this group is very high, these elements have little tendency to form trivalent ions. **6.** Electropositive or metallic character: The elements of group 13 are less electropositive as compared to the elements of groups 1 and 2 (s-block elements). This is due to their small size and high ionisation energy.

The electropositive character increases from boron to aluminium and then decreases from aluminium to thallium. Boron having very high ionisation energy is regarded as a semimetal. It is more closer to non-metals. Aluminium is a metal and is most electropositive. The increase in electropositive nature from B to Al is due to increased atomic size. The remaining three elements Ga, In and Tl are less electropositive and less metallic than aluminium and there is decrease from Ga to Tl. The presence of  $d^{10}$ -electrons in the penultimate shell in gallium and indium and  $d^{10}$  and  $f^{14}$ -electrons in the inner shells of thallium do not shield the nuclear charge effectively and therefore, these elements are less electropositive. Boron is a bad conductor while aluminium is a very good conductor of electricity. Gallium, indium and thallium also conduct electricity.

- 7. Oxidation potential (Reducing nature): Boron does not form positive ions in aqueous solution and thus has low value of oxidation potential. The oxidation potential values of other elements of the group are quite high. This is due to high heats of hydration on account of small size of trivalent cations  $(M^{3+})$ . [Aluminium is a strong reducing agent and in fact better than carbon. This is due to low ionisation energy of aluminium than carbon.]
- **8.** Oxidation states: It is in group 13 that we first encounter elements possessing more than one oxidation state. As  $s^2p^1$  grouping is present in the outermost energy shell of the elements of the group IIIA, the expected oxidation states are +3 and +1. Boron shows +3 oxidation state in all its compounds. Other members show +3 and +1 oxidation states. The stability of +1 oxidation state increases from aluminium to thallium and the stability of +3 oxidation state decreases from aluminium to thallium, *i.e.*, +3 is more important oxidation state for Al, Ga and In whereas +1 oxidation state is more important for Tl.

Relative stability of  $M^+$  and  $M^{3+}$  ions may be give as:

$$B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$$
  
 $B^{+} < Al^{+} < Ga^{+} < In^{+} < Tl^{+}$ 

 $\mathrm{Tl}^+$  ions are more stable than  $\mathrm{Tl}^{3+}$  ions and thus,  $\mathrm{Tl}^{3+}$  ions change to  $\mathrm{Tl}^+$  ions thereby acting as oxidising agents.

$$Tl^{3+}$$
 compounds + 2e  $\longrightarrow$   $Tl^{+}$  compounds (Less stable oxidising agent) (More stable reducing agent)

[Tl(I) compounds resemble alkali metal compounds. Tl(OH) like NaOH is soluble in water and the solution is strongly alkaline. Like alkali metals,  $Tl_2SO_4$  forms a double sulphate with  $Al_2(SO_4)_3$ .

 $K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O;$   $Tl_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$   $Tl_2CO_3$  like  $Na_2CO_3$  is soluble in water.]

In case of Ga and In, +3 oxidation is more stable than +1 oxidation state. The salts of both Ga<sup>+</sup> and In<sup>+</sup> undergo disproportionation reactions in aqueous solutions.

$$\begin{array}{ccc}
+1 & 0 & +3 \\
3GaX & \longrightarrow & 2Ga + GaX_3 \\
3InX & \longrightarrow & 2In + InX_3
\end{array}$$

The decreasing stability of +3 is due to increase in inert pair effect.

Gallium appears to show +2 oxidation state in GaCl<sub>2</sub>. However, it is believed that this compound has the structure Ga[GaCl<sub>4</sub>] which contains univalent and trivalent gallium ions.

$$Ga[GaCl4] = Ga+[Ga3+Cl4]-$$

- **9. Nature of bonding:** The following points suggest that bonding in the compounds of group IIIA elements should be covalent.
- (a) Small size of ions and their high charge are responsible for high polarisation.
  - (b) The sum of first three ionisation energies is very large.
- (c) The electronegativity values are higher and thus, when reacting with other elements the difference is not large.

Boron is considerably smaller than other members and its ionisation potential is maximum and hence it always shows covalency. Many simple compounds of the other elements such as AlCl<sub>3</sub> and GaCl<sub>3</sub> are covalent when anhydrous. However, Al, Ga, In and Tl all form metal ions in solution. The change from covalent to ionic occurs because the ions are highly hydrated and the amount of hydration energy evolved exceeds the ionisation energy. For example, AlCl<sub>3</sub> releases 5808 kJ mol<sup>-1</sup> of hydration energy which exceeds the ionisation energy  $(Al \rightarrow Al^{3+} = 5137 \text{ kJ mol}^{-1})$ , so AlCl<sub>3</sub> ionises. The hydrated aluminium compounds which are regarded as ionic do not contain the aluminium ion,  $Al^{3+}$ , as such but the hexa-aquaaluminium ion,  $[Al(H_2O)_6]^{3+}$ . The relative stability of [M(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> ions decreases on moving down the group. Thallium compounds are ionic. Monovalency of thallium is due to increasing reluctance of the paired ns electrons to form bonds. [Such inertness of ns electrons is observed when the electrons are in fifth or higher energy shell and their removal does not form a cation whose electronic configuration is that of an inert gas. This behaviour is termed as inert pair effect.]

In trivalent state, the number of electrons around the central atom in a molecule such as BCl<sub>3</sub>, BF<sub>3</sub>, AlCl<sub>3</sub>, etc., will be only six and thus behave as **electron deficient molecules**. They act as **Lewis acids**.

$$Cl_3B + : NH_3 \longrightarrow Cl_3B \longleftarrow NH_3$$
Base

However, Lewis acid character decreases down the group as the atomic size increases.

The electron deficient compounds remove their electron deficiency by :

(i) **Back-bonding:** In B $X_3$ , B is  $sp^2$  hybridised *i.e.*, it has one p-orbital vacant. X-atom has filled p-orbital. They overlap resulting into  $\pi$ -bonding.

(ii) Coordination with Lewis bases: B has vacant p-orbital which accepts electron pair from donor.

For example, 
$$BF_3 + F^- \longrightarrow BF_4$$
  
 $Al(OH)_3 + OH^- \longrightarrow Al(OH)_4^-$ 

(iii) **Polymerization :** Some compounds remove electron deficiency by dimerization.

For example, 
$$2AlCl_3 \longrightarrow Al_2Cl_6$$

Note: In aluminium compounds back bonding is not possible due to following reasons:

- (a) p-orbital of Al is large, so p-p overlap is not effective.
- (b) 8-electron core in Al causes larger repulsion, thus destabilising back bonding.
- **10.** Complex formation: Group IIIA elements form complexes much more readily than the s-block elements, because of their smaller size, increased charge and availability of vacant orbitals.
- 11. Reactivity towards air: Boron exists in two forms (a) crystalline and (b) amorphous. Boron is unreactive towards air in crystalline state. Amorphous boron on heating in air form boron trioxide. At high temperatures, it also combines with nitrogen.

$$4B + 3O_2 \xrightarrow{-700^{\circ}C} 2B_2O_3$$

$$2B + N_2 \xrightarrow{\text{High temp.}} 2BN$$

Aluminium is not affected by dry air. However, a thin oxide layer\* is formed on the surface of aluminium metal in moist air. It protects the metal from further attack. It also forms nitride with nitrogen at high temperatures.

$$4Al + 3O_2 \xrightarrow{\text{Heat}} 2Al_2O_3$$
$$2Al + N_2 \xrightarrow{\text{High temp.}} 2AlN$$

Gallium and indium are not affected by air. Thallium forms an oxide layer on its surface. Thallium is preserved under oil or by smearing with vaseline.

12. Reactivity towards water: Boron is not affected by water or steam, however, steam reacts at red heat. Aluminium decomposes cold water if the oxide layer is not present on its surface.

$$2B + 3H2O \longrightarrow B2O3 + 3H2$$
$$2Al + 3H2O \longrightarrow Al2O3 + 3H2$$

<sup>\*</sup>The oxide film on the surface of aluminium is so useful that in industry it is purposely increased by an electrolytic process called **anodising.** Anodised cooking vessels are used now as non-stick cookware.

The tendency of accepting electron pair is also observed in the halides of aluminium and other members (act as Lewis acids). However, this tendency decreases with the increase in size of the cation. They form complex halides of the type  $[MX_6]^{3-}$  where the M-atom extends its coordination number to 6 by the use of d-orbitals. These halides do not show back bonding due to increase in the size of the element. However, they make use of vacant p-orbital by coordinate bond, i.e., complete their octet by forming dimers.

Dimer forms exist in vapour state and in non-polar solvents. Dimer structure disappears when the halides are dissolved in water. This is due to high hydration energy when  $[M(H_2O)_6]^{3+}$  and  $3X^-$  ions are formed making the solution as good conductor of electricity.

The solution becomes acidic owing to hydrolysis.

$$AlCl_3 + 9H_2O \longrightarrow [Al(H_2O)_6](OH)_3 + 3H^+ + 3Cl^-$$

In addition to trihalides, these elements form di as well as monohalides. Boron forms dihalides,  $B_2X_4$ .

$$X$$
  $B-B$   $X$ 

In solid state,  $B_2X_4$  has planar structure but in liquid and vapour state, it has non-eclipsed structure.

Tetrahalides can be synthesised by heating trihalides with mercury at low pressure.

$$2BCl_3 + 2Hg \xrightarrow{Electric \ discharge} B_2Cl_4 + Hg_2Cl_2$$

Gallium and indium also form dihalides. Gallium dihalide is more properly represented as  $Ga^{+}[GaCl_{4}]^{-}$  showing gallium in +1 and +3 oxidation states.

The elements of IIIA in gaseous state form monohalides, MX. These are very unstable halides and they are covalent in nature. The covalent nature decreases and thallium halides are ionic in nature.

### 8.2 ABNORMAL BEHAVIOUR OF BORON

Boron differs markedly from the rest of the members of group IIIA and this abnormal behaviour is illustrated in the following properties:

(i) Boron has very small atomic radii, hence greater nuclear attraction on the outermost electrons. It has very high ionisation energy. This gives boron distinctly **nonmetallic** character while the rest are metals.

- (ii) Boron has maximum covalency of four due to nonavailability of d-orbitals while the rest have maximum covalency of six.
  - (iii) Boron alone exhibits allotropy.
- (iv) Boron shows +3 oxidation state while others can show +1 and +3 oxidation states.
- (v) Boron does not form cations in aqueous solution as the hydration energy is less than sum of three successive ionisation energies.
- (vi) Boron halides are monomeric while the halides of the other elements are dimeric. It does not show inert pair effect.
- (vii) Boron forms a number of volatile hydrides which are electron deficient compounds. Others form only one polymeric hydride. Thallium does not form hydride.
- (viii) Boron does not decompose water or steam while other elements decompose hot water or steam.
- (ix) The oxide of boron, B<sub>2</sub>O<sub>3</sub>, is acidic in nature while the similar oxides of the other elements are either amphoteric or basic.
- (x) Boron is not attacked by non-oxidising acids while other elements are attacked.
- (xi) Boron dissolves in conc. HNO<sub>3</sub> forming H<sub>3</sub>BO<sub>3</sub>. The other elements become passive specially Al and Ga.
- (xii) Boron combines with metals and form borides while other elements do not combine. They can form alloys.

### 8.3 COMPARISON OF BORON AND ALUMINIUM

Since both boron and aluminium have three electrons in their valency shell, they have many similarities in their properties.

B 5 2, 3 
$$1s^2$$
,  $2s^2$   $2p^1$  [He]  $2s^2$   $2p^1$   
Al 13 2, 8, 3  $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^2$   $3p^1$  [Ne]  $3s^2$   $3p^1$ 

On the other hand, they have different number of electrons in their penultimate shell (2 in boron and 8 in aluminium) and consequently show many dissimilarities also.

### Points of Similarities

- (i) Electronic configuration: Both have same number of electrons in the outermost shell (valency shell).
- (ii) Valency: Both show trivalency. They do not show variable valency because their kernels are stable. It is difficult to get B<sup>3+</sup> because large amount of energy is required and therefore boron forms tri-covalent compounds. Aluminium also forms covalent compounds. It can, however, form electrovalent compounds when it combines with strong electron accepting atoms or groups. The size of Al<sup>3+</sup> ion is very small. On account of small size and high charge, it has high polarising power. This accounts for a covalent character even in the case of electrovalent compounds, for example, AlCl<sub>3</sub>, AlBr<sub>3</sub> and AlI<sub>3</sub> have covalent nature.
- (iii) Oxidation state: Both show common oxidation state of +3 in majority of their compounds.

Compound	Oxid. state	Compound	Oxid. state
$B_2O_3$	. +3	$Al_2O_3$	+3
BCl <sub>3</sub>	+3	AlCl <sub>3</sub>	+3
$H_3BO_3$	+3	$Al(OH)_3$	+3
$Na_2B_4O_7$	+3	NaAlO <sub>2</sub>	+3

Boron, however, also shows an oxidation state of -3 in the metal borides, e.g., in  $Mg_3B_2$  (magnesium boride), oxidation state of boron is -3.

(iv) Action of alkalies: Both dissolve in alkalies and evolve hydrogen.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$
 Sodium borate 
$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$$
 Sodium meta aluminate

(v) Action of concentrated  $H_2SO_4$ : Both react with conc.  $H_2SO_4$  and evolve sulphur dioxide,  $SO_2$ .

$$[H_2SO_4 \longrightarrow H_2O + SO_2 + O] \times 3$$

$$2B + 3O \longrightarrow B_2O_3$$

$$B_2O_3 + 3H_2O \longrightarrow 2H_3BO_3$$

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$

$$6H_2SO_4 + 2A1 \longrightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$$

(vi) Formation of oxides: Both form oxides of the type  $M_2O_3$  when heated in atmosphere of oxygen at high temperature.

$$4B + 3O_2 \xrightarrow{700^{\circ}C} 2B_2O_3$$
 (Boron oxide or boric anhydride)

$$4Al + 3O_2 \xrightarrow{800^{\circ}C} 2Al_2O_3$$
 (Aluminium oxide or alumina)

The oxides are amphoteric in nature. B<sub>2</sub>O<sub>3</sub> is more acidic and less basic while Al<sub>2</sub>O<sub>3</sub> is more basic and less acidic.

$$\begin{array}{c} B_2O_3 + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2O \\ Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O \\ Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O \end{array}$$

(vii) Formation of chlorides: Both form trichlorides either by passing chlorine over heated boron or aluminium or by passing chlorine over heated mixture of their oxides and charcoal.

$$2B + 3Cl2 \longrightarrow 2BCl3$$

$$2Al + 3Cl2 \longrightarrow 2AlCl3$$

$$B2O3 + 3C + 3Cl2 \longrightarrow 2BCl3 + 3CO$$

$$Al2O3 + 3C + 3Cl2 \longrightarrow 2AlCl3 + 3CO$$

Trichlorides are hydrolysed by water, i.e., both show covalent nature.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$
  
 $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$ 

Halides act as Lewis acids whenever donor molecules (Lewis bases) are available.

$$H_3N \longrightarrow BCl_3, H_3N \longrightarrow AlCl_3$$

(viii) Formation of nitrides: Both form nitrides of the type MN when heated in the atmosphere of nitrogen or ammonia.

$$2B + N_2 \longrightarrow 2BN$$

$$2B + 2NH_3 \longrightarrow 2BN + 3H_2$$

$$2Al + N_2 \longrightarrow 2AlN$$

$$2Al + 2NH_3 \longrightarrow 2AlN + 3H_2$$

The nitrides undergo hydrolysis with steam.

AlN + 3H<sub>2</sub>O 
$$\longrightarrow$$
 Al(OH)<sub>3</sub> + NH<sub>3</sub> Aluminium hydroxide

(ix) Formation of sulphides: Both form sulphides of the type  $M_2S_3$  when heated with sulphur.

$$2B + 3S \longrightarrow B_2S_3$$
  
 $2Al + 3S \longrightarrow Al_2S_3$ 

Sulphides are hydrolysed with water.

$$\begin{array}{ll} B_2S_3 + 6H_2O & \longrightarrow 2H_3BO_3 + 3H_2S \\ Al_2S_3 + 6H_2O & \longrightarrow 2Al(OH)_3 + 3H_2S \end{array}$$

(x) Formation of alkyl compounds: Both form similar types of alkyl compounds, such as B(CH<sub>3</sub>)<sub>3</sub>, Al(CH<sub>3</sub>)<sub>3</sub>.

$$2BCl_3 + 3Zn(CH_3)_2 \longrightarrow 2B(CH_3)_3 + 3ZnCl_2$$
  
 $2Al + 3Hg(CH_3)_2 \longrightarrow 2Al(CH_3)_3 + 3Hg$ 

(xi) Reducing nature: Both act as powerful reducing agents.

$$\begin{array}{ccc} 4B + 3CO_2 & \longrightarrow 2B_2O_3 + 3C \\ 3SiO_2 + 4B & \longrightarrow 2B_2O_3 + 3Si \\ 2Al + Cr_2O_3 & \longrightarrow Al_2O_3 + 2Cr \\ 2Al + Fe_2O_3 & \longrightarrow Al_2O_3 + 2Fe \\ 4Al + 3CO_2 & \longrightarrow 2Al_2O_3 + 3C \end{array}$$

(xii) Action of steam: Boron reacts with steam at red heat liberating hydrogen.

$$2B + 3H_2O \longrightarrow B_2O_3 + 3H_2$$

Aluminium decomposes boiling water.

$$2Al + 6H2O \longrightarrow 2Al(OH)3 + 3H2$$

### Dissimilarities between Boron and Aluminium

Boron and aluminium show dissimilarities in properties due to difference in their electronic configuration, size and ionisation potential. Main points of difference are given in the table.

	<u> </u>	
Boron	Aluminium	
(i) Boron is a non-metal.	Aluminium is a metal.	
(ii) It is a bad conductor of heat and electricity.	It is a good conductor of heat and electricity.	
(iii) It has high melting point (m.pt. 2300°C).	It has low melting point (m.pt. 660°C).	
(iv) Boron shows allotropy. The allotropic forms are crystalline boron	Aluminium does not show allotropy.	15
and amorphous boron,		:

(v) It does not react with dil. HCl and dil. H2SO4.

(vi) It is attacked by conc. HNO3.

$$[2HNO_{3} \longrightarrow H_{2}O + 2NO_{2} + O] \times 3$$

$$2B + 3O \longrightarrow B_{2}O_{3}$$

$$B_{2}O_{3} + 3H_{2}O \longrightarrow 2H_{3}BO_{3}$$

$$2B + 6HNO_{3} \longrightarrow 2H_{3}BO_{3} + 6NO_{2}$$
or
$$B + 3HNO_{3} \longrightarrow H_{3}BO_{3} + 3NO_{2}$$

- (vii) Borates are very stable.
- (viii) BCl3 is a fuming liquid.
- (ix) It combines with metals. The compounds formed are called borides.  $3Mg+2B \longrightarrow Mg_3B_2$
- (x) B(OH)<sub>3</sub> is a weak acid.
- (xi) The maximum covalency of boron is four and is shown in compounds like potassium fluoroborate, K[BF<sub>4</sub>].
- (xii) Boron forms a number of hydrides like  $B_2H_6$ ,  $B_4H_{10}$ ,  $B_{10}H_{14}$ , etc. These are covalent and electron deficient in nature.
- (xiii) Boron trihalides exist as discrete molecules, *i.e.*, monomeric in nature, BX<sub>3</sub>
- (xiv) It forms covalent compounds only.
- (xv) It forms a covalent carbide, B<sub>4</sub>C.

### DIAGONAL RELATIONSHIP OF BORON AND SILICON

Following are the properties where boron and silicon show close resemblance:

- (i) Both boron and silicon are non-metals. Both have high melting points  $[B = 2300^{\circ}C; Si = 1410^{\circ}C]$ , high ionisation energies (B = 8.3 eV, Si = 8.20 eV) and are bad conductors of electricity at normal temperature. However, the conductance improves as the temperature increases. Hence, both are semiconductors.
- (ii) Both have nearly equal densities, electronegativities [Density  $B = 3.30 \text{ g mL}^{-1}$ ;  $Si = 3.52 \text{ g mL}^{-1}$ ; Electronegativity B = 2.0; Al = 1.8]
  - (iii) Both boron and silicon show allotropy.
- (iv) Both boron and silicon do not form cations as their ionisation energy is very high.
- (v) Most of the compounds of boron and silicon are covalent.
- (vi) Boron and silicon burn in air on heating forming stable oxides B<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> respectively. The oxides are acidic and combine with alkalies forming borates and silicates respectively.

$$\begin{array}{ccc} & B_2O_3 + 2NaOH \longrightarrow 2NaBO_2 + H_2O \\ or & B_2O_3 + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2O \\ & SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O \end{array}$$

(vii) Both boron and silicon combine with metals to form borides and silicides respectively.

It dissolves in HCl and H<sub>2</sub>SO<sub>4</sub> (dil.) evolving hydrogen.

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2$$

It becomes passive with conc. HNO<sub>3</sub>. A thin layer of Al<sub>2</sub>O<sub>3</sub> is formed on the surface which makes the metal inert.

Aluminates are less stable.

AlCl<sub>3</sub> is a solid.

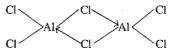
It forms alloys with metals.

Al(OH)3 is amphoteric in nature.

Aluminium has a maximum covalency of six which is shown in compounds like Na<sub>3</sub>[AlF<sub>6</sub>]. This is due to the involvement of *d*-orbitals of the valency shell.

It does not form any stable and definite hydride. A polymeric hydride (AlH<sub>3</sub>)<sub>x</sub> has been reported.

Aluminium trihalides like AlCl<sub>3</sub>, AlBr<sub>3</sub> exist as dimers both in vapour state and in non-polar solvents as shown below.



It forms both covalent and electrovalent compounds.

It forms an ionic carbide, Al<sub>4</sub>C<sub>3</sub>, which on hydrolysis evolves CH<sub>4</sub>.

$$2B + 3Mg \longrightarrow Mg_3B_2$$
  
Si +  $2Mg \longrightarrow Mg_2Si$ 

(viii) Both do not directly combine with hydrogen. However, both form a number of hydrides. Hydrides are formed by almost identical manner. All are covalent hydrides.

$$Mg_3B_2 \xrightarrow{Dil.HCl}$$
 a mixture of boron hydrides  $Mg_2Si \xrightarrow{Dil.HCl}$  a mixture of silicon hydrides  $4BCl_3 + 3LiAlH_4 \longrightarrow 3LiCl + 3AlCl_3 + 2B_2H_6$   $SiCl_4 + LiAlH_4 \longrightarrow LiCl + AlCl_3 + SiH_4$ 

[Note: Boron hydrides (boranes) are electron deficient while silicon hydrides (silanes) are saturated compounds.]

(ix) Orthoboric acid  $(H_3BO_3)$  and ortho silicic acid  $(H_4SiO_4)$  form esters when treated with alcohols in presence of  $H_2SO_4$ .

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{H_2SO_4} (C_2H_5)_3BO_3 + 3H_2O$$
Triethyl borate

 $H_4SiO_4 + 4C_2H_5OH \xrightarrow{H_2SO_4} (C_2H_5)_4SiO_4 + 4H_2O$ 
Tetraethyl silicate

[Note: The vapours of triethyl borate burn with green edged flame. This is the qualitative test of borates.]

(x) Halides of boron and silicon are hydrolysed.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$
  
 $SiCl_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HCl$ 

Both form complex halides.

$$BF_3 + HF \longrightarrow H[BF_4]$$
  
 $SiF_4 + 2HF \longrightarrow H_2[SiF_6]$ 

(xi) Both react with fused alkalies and evolve hydrogen.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2 \uparrow$$
  
Si +  $2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2 \uparrow$ 

(xii) Both combine with carbon to form carbides B<sub>4</sub>C and SiC. These are very hard substances and are used for cutting and abrasing purposes.

### 8.5 BORON

**Occurrence:** Boron is not found free in nature. In the combined state, it is found as the salts of boric acid. The important minerals of boron are:

(i) Borax (Tincal) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O—It is found in Tibet, Ceylon,

California and Kashmir.

(ii) Colemanite  $Ca_{2}B_{6}O_{11}\cdot 5H_{2}O \text{---It is found in Asia Minor}$ 

and America.
Panderinite Ca<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·31

 $\begin{array}{ll} \text{Panderinite} & \text{Ca}_2B_6O_{11}\cdot 3H_2O \\ \text{(iii)} \ \, \text{Boracite} & 2Mg_3B_8O_{15}\cdot MgCl_2\text{—It is found in Stass-furt,} \end{array}$ 

Germany

(iv) Boronatro calcite CaB<sub>4</sub>O<sub>7</sub>·NaBO<sub>2</sub>·8H<sub>2</sub>O—It is found in Chile.

(v) Kernite (Rasorite) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·4H<sub>2</sub>O—It is found in Mojave desert

in America.

(vi) Boric acid H<sub>2</sub>BO<sub>3</sub>—It

id H<sub>3</sub>BO<sub>3</sub>—It occurs in the jets of steam called

soffioni escaping from ground in the volcanic

regions of Tuscany.

Boron is also present to some extent in plants and sometimes in coal ash.

**Extraction:** Boron is extracted from borax and colemanite minerals. The extraction involves two steps:

- (i) Preparation of boric anhydride, B<sub>2</sub>O<sub>3</sub>, from one of the minerals.
- (ii) Reduction of B<sub>2</sub>O<sub>3</sub>, to an impure brown, amorphous form of boron.

### 3 1st Step

(a) Preparation of B<sub>2</sub>O<sub>3</sub> from borax: The finely ground borax is heated with concentrated hydrochloric acid or concentrated sulphuric acid when sparingly soluble orthoboric acid, H<sub>3</sub>BO<sub>3</sub> separates out.

$$\begin{array}{c} Na_2B_4O_7 + 2HCl & \longrightarrow 2NaCl \ + \ H_2B_4O_7 \\ Borax & Tetraboric \ acid \\ Na_2B_4O_7 + H_2SO_4 - \longrightarrow Na_2SO_4 + H_2B_4O_7 \\ H_2B_4O_7 + 5H_2O & \longrightarrow 4H_3BO_3 \\ Orthoboric \ acid \\ \end{array}$$

Orthoboric acid is strongly heated to get  $B_2O_3$ .  $2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$ 

### (b) Preparation of B<sub>2</sub>O<sub>3</sub> from colemanite:

(i) The powdered mineral is fused with sodium carbonate.

$$\begin{array}{c} Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2 \\ \text{Colemanite} & \text{Borax} & \text{Sodium} \\ \text{metaborate} \end{array}$$

The fused mass is extracted with hot water. CaCO<sub>3</sub> remains as insoluble. The filtrate containing borax and sodium metaborate is put to crystallisation when borax is obtained. The remaining solution is treated with carbon dioxide which converts sodium metaborate into borax.

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

The borax is then converted into B<sub>2</sub>O<sub>3</sub> in the manner described above.

(ii) The other method of conversion of colemanite into  $B_2O_3$  involves the suspension of mineral in water and passing of sulphur dioxide gas into the suspension.

$$Ca_2B_6O_{11} + 4SO_2 + 4H_2O \longrightarrow 2Ca(HSO_3)_2 + H_4B_6O_{11} + 7H_2O \longrightarrow 6H_3BO_3$$

$$Ca_2B_6O_{11} + 11H_2O + 4SO_2 \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$$

On concentration and cooling, crystals of boric acid separate out. These crystals form  $B_2O_3$  on strong heating.

$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

### 3 2nd Step

**Reduction of B\_2O\_3:** The reduction of boric anhydride  $(B_2O_3)$ , can be done with sodium, potassium or magnesium. The boric anhydride is mixed with sodium, potassium or magnesium powder and heated in a covered crucible.

$$\begin{array}{c} B_2O_3 + 6Na \longrightarrow 2B + 3Na_2O \\ B_2O_3 + 6K \longrightarrow 2B + 3K_2O \\ B_2O_3 + 3Mg \longrightarrow 2B + 3MgO \end{array}$$

The fused mass is stirred with iron rod as to oxidise the unreacted sodium or potassium. The mass is then boiled with dil. HCl when insoluble boron powder is obtained. It is washed with water and made dry. This is the amorphous variety of boron.

Amorphous boron of low purity is often known as Moissan boron. It is about 95–98% pure and impurities are chiefly metal borides. It is black in colour.

Modern method (Electrolytic method): Boron is obtained these days by the electrolysis of a fused mixture containing boric anhydride, magnesium oxide and magnesium fluoride at 1100°C. The electrolysis is done in carbon crucible which acts as anode and iron rod is used as cathode. The magnesium discharged at cathode reduces B<sub>2</sub>O<sub>3</sub> to boron.

$$2MgO \longrightarrow 2Mg + O_2$$
  
 $B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$ 

Boron thus obtained is heated electrically in vacuum at 1100°C when the impurities are volatilised off and pure boron is obtained.

Crystalline variety of boron is obtained by the reduction of  $B_2O_3$  with aluminium powder.

$$B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3$$

Aluminium is removed by heating the fused mass with NaOH solution.

High purity crystalline boron can also obtained by doing reduction of boron tribromide with hydrogen on tungsten wire at 1200°C.

$$2BBr_3 + 3H_2 \xrightarrow{W \text{ wire}} 2B + 6HBr$$

### **Physical Properties**

Elemental boron exists in two allotropic forms, (a) grey black, nonmetallic, high-melting point crystalline solid and (b) a dark brown amorphous powder with a structure based on clusters of 12 atoms Fig. 8.2. Crystalline boron is black and chemically inert in nature. It is very hard in nature. Amorphous boron is chemically brown and active. It melts at 2300°C

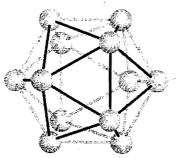


Fig. 8.2 The structure of boron is based on linked 12-atom units. The unit has 20 faces, so it is called an icosahedron

and boils at 2550°C. It is difficult to fuse it. It is bad conductor of heat and electricity. Its density is 2.4 g mL<sup>-1</sup>.

### **Chemical Properties**

(i) Reaction with air and oxygen: The element is very inert and is attacked by only the strongest oxidizing agents. Amorphous form when heated in air or oxygen at 700°C, burns with a reddish flame forming a mixture of oxide and nitride.

$$4B + 3O_2 \longrightarrow 2B_2O_3$$
  
 $2B + N_2 \longrightarrow 2BN$ 

(ii) Reaction with water: Boron is not affected by water under ordinary conditions, however, when steam is passed over red hot boron, hydrogen is liberated.

$$2B + 3H2O \longrightarrow B2O3 + 3H2\uparrow$$

(iii) Reaction with acids: Boron is not affected by nonoxidising acids. It is attacked by oxidising acids like conc.  $H_2SO_4$  and  $HNO_3$ .

B + 3HNO<sub>3</sub> 
$$\longrightarrow$$
 H<sub>3</sub>BO<sub>3</sub> + 3NO<sub>2</sub> $\uparrow$   
2B + 3H<sub>2</sub>SO<sub>4</sub>  $\longrightarrow$  2H<sub>3</sub>BO<sub>3</sub> + 3SO<sub>2</sub>  $\uparrow$ 

(iv) Reaction with alkalies: Boron dissolves in fused alkalies, liberating hydrogen.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2\uparrow$$

(v) Reaction with metals: Boron combines with strongly electropositive metals at high temperatures to form borides.

$$3Mg + B_2 \longrightarrow Mg_3B_2$$

(vi) Reaction with non-metals: Boron forms  $B_2S_3$  when heated with sulphur. It forms extremely hard substance boron

carbide  $(B_4C)$ , when heated with carbon in an electric furnace. Boron combines directly with chlorine and bromine at higher temperatures.

(vii) Reducing nature: It is a powerful reducing agent.

$$4B + 3CO_2 \longrightarrow 2B_2O_3 + 3C$$
  
 $4B + 3SiO_2 \longrightarrow 2B_2O_3 + 3Si$ 

#### Uses

Boron is used:

- (i) as a deoxidiser in the casting of copper.
- (ii) for making boron steels which are very hard and are used as control rods in atomic reactors.
  - (iii) as a catalytic agent.
- (iv) When boron fibres are incorporated in plastics, the result is a very tough material that is stiffer than steel yet lighter than aluminium and used in aircraft, missiles and body armour.
- (v) Boron steel or boron carbide rods are used to control the nuclear reactions. Boron has a very high cross-section to capture the neutrons. According to another concept boron absorbs neutron to make the boron having even number of neutrons.

$$_5B^{10} + _0n^1 \longrightarrow _5B^{11}$$

(vi) Boron is absolutely necessary as micronutrient for some green plants in trace amounts, but there is a relatively narrow concentration range above which boron is toxic to most plants. Boron production remains quite low despites the element's desirable properties of hardness and lightness.

### 8.6 COMPOUNDS OF BORON

### **■ 1. Boron Trioxide, B<sub>2</sub>O<sub>3</sub>**

It is also called sesquioxide. It is an anhydride of orthoboric acid.

It is prepared by burning boron in oxygen,

$$4B + 3O_2 \longrightarrow 2B_2O_3$$

or heating orthoboric acid to redness,

$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

### **Properties**

It is a white hygroscopic solid. It absorbs moisture (becoming opaque from transparent glassy mass) and finally converted into boric acid.

$$B_2O_3 + H_2O \longrightarrow 2HBO_2$$
 $Metaboric acid$ 
 $HBO_2 + H_2O \longrightarrow H_3BO_3$ 
Orthoboric acid

 $B_2O_3$  is, thus, the anhydride of orthoboric acid.

It is an acidic oxide. It combines with metal oxides when fused and forms metaborates. Some of the metaborates have characteristic colours (this is the basis of borax bead test).

$$CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$$

[The volatile part of the salt is displaced by 
$$B_2O_3$$
.

 $CuO \cdot SO_3 + B_2O_3 \longrightarrow CuO \cdot B_2O_3 + SO_3$ 
 $(CuSO_4)$ 
 $Blue bead$ 
 $[Cu(BO_2)_2]$ 
 $Cr_2O_3 \cdot 3SO_3 + 3B_2O_3 \longrightarrow Cr_2O_3 \cdot 3B_2O_3 + 3SO_3]$ 
 $[Cr_2(SO_4)_3]$ 
 $Green bead$ 
 $[2Cr(BO_2)_3]$ 

It is reduced by magnesium.

$$B_2O_3 + 3Mg \xrightarrow{Heated} 2B + 3MgO$$

When reacted with strongly acidic oxides, it behaves as a base.

$$2B_2O_3 + P_4O_{10} \longrightarrow 4BPO_4$$

### Uses

Boron oxide, B<sub>2</sub>O<sub>3</sub> is used in glass industry with composition SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and small amount of Al<sub>2</sub>O<sub>3</sub>, to lower the coefficient of thermal expansion. The coefficient of thermal expansion is appreciably lower in certain borosilicate glasses, in which many of the silicon sites are occupied by boron. "Pyrex" and "Kimex" are most familiar of these glasses, has a coefficient of linear expansion about one third that of ordinary soda-lime glass, Because borosilicate glasses do not expand much when heated, they survive rapid heating and cooling and so far is the material of choice for laboratory glassware and household ovenware.

### 2: Borax (Sodium Tetraborate) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O

### **Preparation**

It is prepared by following methods:

- (i) Borax occurs naturally in dried up inland lakes of Tibet, Ceylon, California (U.S.A.) and India. In India, it is found in Laddakh and Puga valley of Kashmir. It is also called *Tincal* or *Suhaga*. Tincal contains about 45% of borax. Advantage is taken of its higher solubility in hot water (101 grams per 100 grams of water at 100°C) against low solubility at 0°C (1.3 grams per 100 grams of water at 0°C) in its purification. The natural tincal is dissolved in hot water and insoluble impurities are filtered off. The solution is concentrated and cooled when crystals of borax are obtained.
- (ii) Borax can be obtained from colemanite mineral (see section 8.5).
- (iii) From boric acid: Small quantities of borax are obtained from boric acid by neutralising it with soda ash.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

### **Properties**

- (i) Borax is known in three forms:
- (a) **Prismatic borax**, which is the common form and is the decahydrate form, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O. It is obtained by crystalli-

sing the solution at ordinary temperature. It is less soluble in cold water but highly soluble in hot water.

- (b) Octahedral form, which is the pentahydrate, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·5H<sub>2</sub>O, is obtained by crystallising solution at 60°C. This is jeweller's borax.
- (c) **Borax glass** is the anhydrous form, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. It is obtained by heating the common form above its melting point. It is a colourless glassy mass and is not stable in moist air as it absorbs moisture and is gradually converted into decahydrate form.
- (ii) Basic nature: The solution of borax is alkaline in nature. This is due to its hydrolysis (salt of strong alkali and weak acid).

$$Na_2B_4O_7 + 7H_2O \Longrightarrow 2NaOH + 4H_3BO_3$$
  
Strong alkali Weak acid

(iii) Action of heat: On heating, borax first swells up due to elimination of water molecules. On further heating, it melts to a liquid which then solidifies to a transparent glassy mass.

$$\begin{array}{c} \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \xrightarrow{\text{Heat}} \begin{array}{c} \text{Na}_2\text{B}_4\text{O}_7 \xrightarrow{740^{\circ}\text{C}} \\ \text{Anhydrous} \end{array} \xrightarrow{\text{Na}_2\text{B}_4\text{O}_7} \xrightarrow{\text{740}^{\circ}\text{C}} \\ \begin{array}{c} \text{2NaBO}_2 \\ \text{Sodium} \\ \text{metaborate} \end{array} \xrightarrow{\text{Boric}} \\ \begin{array}{c} \text{Boric} \\ \text{anhydride} \end{array}$$

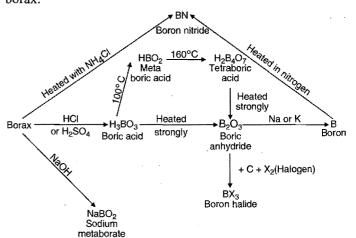
When hot glassy mass is brought in contact with a coloured salt and heated again in the flame, B<sub>2</sub>O<sub>3</sub> displaces the volatile oxides and combines with basic oxides to form metaborates. Metaborates of basic radicals have characteristic colours.

$$CuSO_4 + B_2O_3 \longrightarrow CuO \cdot B_2O_3 + SO_3$$

$$\downarrow \qquad \qquad Cu(BO_2)_2$$
Blue

This is the chemistry of borax bead test.

(iv) Various compounds of boron can be obtained from borax.



(v) Aqueous solution of borax acts as a buffer because it contains weak acid and its salt with strong base.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2Na[B(OH)_4] + 2H_3BO_3$$

**Structure of Borax:** Borax can be represented as  $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$ . It has two tetrahedral and two triangular units joined together as shown in following figure.

#### Uses

Borax is used:

- (i) for the borax bead test in qualitative analysis.
- (ii) as a flux. (This is based on its property to dissolve many metal oxides to form borates of low melting points.)
  - (iii) as an antiseptic.
- (iv) in water softening as it forms insoluble calcium and magnesium borates (CaB<sub>4</sub>O<sub>7</sub>, MgB<sub>4</sub>O<sub>7</sub>).
- (v) in the manufacture of enamels and glazes for pottery and tiles.
- (vi) in making optical glasses and also borosilicate glass which is very resistant to heat and shock.
  - (vii) in leather industry for cleaning hides and skins.
  - (viii) for impregnating match-sticks to prevent after glow.
  - (ix) for glazing paper and playing cards.
  - (x) for stiffening of candles.

### 3. Orthoboric Acid, H<sub>3</sub>BO<sub>3</sub>

#### Preparation

(i) From borax: A hot concentrated solution of borax is treated with calculated quantity of concentrated sulphuric acid. When the solution is cooled, crystals of boric acid are obtained.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

(ii) From colemanite: A large quantity of boric acid is made from colemanite mineral. The mineral is powdered and mixed with boiling water. Sulphur dioxide is circulated through the suspension when boric acid is formed.

 $Ca_2B_6O_{11} + 2SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$ On cooling, boric acid crystallises out.

(iii) From Tuscany soffioni: Boric acid occurs in the jets of steam called soffioni issuing from the ground in the volcanic regions of Tuscany. The jets are caught in large tanks of water. The resulting liquid is concentrated by steam. On allowing the hot solution to cool, crystals of boric acid separate out.

#### **Properties**

(i) It forms soft, white, needle like crystals having a soapy touch.

- (ii) It is less soluble in cold water but more soluble in hot water. It is steam volatile.
- (iii) It is a weak  $(K_a = 1 \times 10^{-9})$  monobasic acid. It does not act as a **proton-donor**, *i.e.*, protonic acid but behaves as a **Lewis acid.** It actually accepts a pair of electrons from OH<sup>-</sup> ion.

$$H \longrightarrow OH + B(OH)_3 \longrightarrow [B(OH)_4]^- + H^+$$

(iv) When heated at 100°C, it loses water and converted into metaboric acid.

$$H_3BO_3 \xrightarrow{100^{\circ}C} HBO_2 + H_2O$$

When metaboric acid is heated at 160°C, tetraboric acid results.

$$4HBO_2 \xrightarrow{160^{\circ}C} H_2B_4O_7 + H_2O$$

On strong heating, B<sub>2</sub>O<sub>3</sub> is formed,

$$H_2B_4O_7 \longrightarrow 2B_2O_3 + H_2O$$

(v) A mixture of ethyl alcohol with boric acid burns with green edged flame due to the formation of volatile ethyl borate.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow B(OC_2H_5)_3 + 3H_2O$$
  
Ethyl borate

#### Uses

Orthoboric acid is used:

- (i) as an antiseptic and eye wash under the name 'boric lotion'.
  - (ii) in the manufacture of enamels and glazes for pottery.
  - (iii) as food preservative.
  - (iv) in glass industry.

**Structure of Boric Acid:** The electronic configuration of boron atom is  $2s^22p^1$ . In the excited state one electron from 2s is promoted to 2p orbital. The three singly occupied orbitals undergo  $sp^2$  hybridisation giving three hybridised orbitals. These three hybridised orbitals overlap individually with p-orbital of  $O^-$  forming three B— $O^-$  bonds.



Trigonal planar structure of BO3 unit

In boric acid, planar  $BO_3^{3-}$  units are joined by hydrogen bonds to give a layered structure as shown in Fig. 8.1.

#### 4. Halides of boron

#### Preparation

Boron combines with halogens and forms the halides of type  $BX_3$ , (X = F, Cl, Br, I).

Except  $BF_3$ , other trihalides can be prepared by the treatment of halogens on a mixture of  $B_2O_3$  and carbon at high temperature.

$$B_2O_3 + 3C + 3X_2 \longrightarrow 2BX_3 + 3CO$$
  
 $(X_2 = Cl_2, Br_2, I_2)$ 

The most important is boron trifluoride, BF<sub>3</sub>, an industrial catalyst produced by the reaction between boric oxide, calcium fluoride, and sulphuric acid.

$$3CaF_2 + B_2O_3 + 3H_2SO_4 \xrightarrow{\Delta} 2BF_3 + 3CaSO_4 + 3H_2O$$
  
Boron trihalides are also obtained by direct combination of

boron and halogens under suitable conditions.

$$2B + 3X_2 \longrightarrow 2BX_3$$

### **Properties**

- (i) These are covalent in nature due to small size and high charge density on B<sup>3+</sup> ion.
- (ii) These are non-electrolytes, as in liquid state do not conduct electricity.
- (iii) The boiling points of halides are very low. The boiling points increase as the atomic number of halogen increases. BF<sub>3</sub> is a colourless gas, BCl<sub>3</sub> is a colourless fuming liquid (b.pt. = 13°C), BBr<sub>3</sub> is also a colourless fuming liquid (b.pt. = 90°C) while BI<sub>3</sub> is a white fusible solid (m.pt. 310°C).
- (iv) The trihalides are electron deficient compounds. The B atom has an incomplete octet in all its halides. Boron atom acquires six electrons on account of three B—X bonds, i.e., 2 electrons short of an octet. Thus, the boron atom in BX<sub>3</sub> molecule can accept two more electrons, i.e., an electron pair from the donor atoms like N, P, O, S, F, etc., in NH<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub>O, H<sub>2</sub>S, HF, F, etc., respectively to form addition compounds (donor-acceptor compounds).

$$\begin{array}{ccc} H_3N \mbox{:} & + & BF_3 & \longrightarrow [H_3N \to BF_3] \\ & \mbox{Donor} & \mbox{Acceptor} \\ (Lewis base) & (Lewis acid) \end{array}$$

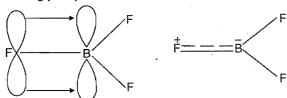
The relative Lewis acid character of boron trihalides is found to follow the following order,

$$BI_3 > BBr_3 > BCl_3 > BF_3$$

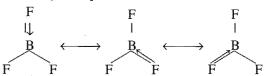
but the expected order on the basis of electronegativity of the halogens (electronegativity of halogens decreases from F to I) should be,

$$BF_3 > BCl_3 > BBr_3 > BI_3$$

This anomaly is explained on the basis of the relative tendency of the halogen atom to back donate its unutilised electrons to vacant p-orbital of boron atom. In BF<sub>3</sub>, boron has a vacant 2p-orbital and each fluorine has fully filled unutilised 2p-orbitals. Fluorine transfers two electrons to vacant 2p-orbital of boron, thus forming  $p\pi$ — $p\pi$  bond.



This type of bond has some double bond character and is known as dative or back bonding. All the three bond lengths are same. It is possible when double bond is delocalized. The delocalization may be represented as:



This bond reduces the electron deficiency of boron atom hence its Lewis acid character decreases. The tendency to form back bonding is maximum in  $BF_3$  and decreases from  $BF_3$  to  $BI_3$ . Thus,  $BCI_3$ ,  $BBr_3$  and  $BI_3$  are stronger Lewis acids than  $BF_3$ .

(v) All boron trihalides, except boron trifluoride, are hydrolysed to boric acid.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

The degree of hydrolysis increases from  $BCl_3$  to  $BI_3$ . Due to resistance of  $BF_3$  to hydrolysis and its tendency to act as Lewis acid,  $BF_3$  is used as a catalyst in organic reactions.

### 5. Hydrides of Boron or Boranes

Boron forms a number of hydrides. These are called boranes by analogy with alkanes. The boranes are an extensive series of highly reactive electron deficient binary compounds of boron and hydrogen, the boranes have three-centre bonds. These belong to one of the two series, viz.,  $B_nH_{n+4}$  and  $B_nH_{n+6}$ . The members of  $B_nH_{n+6}$  are less stable.

$B_nH_{n+4}$	$B_nH_{n+6}$
$B_2H_6$	$B_{4}H_{10}$
$B_5H_9$	$B_5H_{11}$
$B_6H_{10}$	$B_6H_{12}$
$B_{10}H_{14}$	$B_9H_{15}$

The simplest boron hydride,  $BH_3$ , is unknown. The most important hydride is diborane ( $B_2H_6$ ) which has been extensively studied.

### Diborane, B<sub>2</sub>H<sub>6</sub>

It is prepared:

(i) by the action of lithium aluminium hydride on boron trichloride in the presence of ether.

$$4BCl_3 + 3LiAlH_4 \xrightarrow{Ether} 2B_2H_6 + 3LiCl + 3AlCl_3$$

(ii) by passing silent electric discharge at low pressure through a mixture of boron trichloride or tribromide and excess of hydrogen.

$$2BCl_3 + 6H_2 \xrightarrow{\text{Silent electric}} B_2H_6 + 6HCl$$

(iii) by reacting lithium hydride with boron trifluoride.

$$8BF_3 + 6LiH \longrightarrow B_2H_6 + 6LiBF_4$$

#### **Properties**

(i) It is a colourless gas which is stable at low temperatures in the absence of moisture and grease. It bursts into flame in air. At higher temperatures, it changes to higher boranes and at red heat it decomposes to hydrogen and pure boron. It has disagreeable odour and causes headache.

$$B_2H_6 \xrightarrow{\text{Red heat}} 2B + 3H_2$$

 $B_2H_6 \xrightarrow{\text{Red heat}} 2B + 3H_2$ (ii) It burns in oxygen. The reaction is highly exothermic.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + X$$

(iii) It readily reacts with water liberating hydrogen.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

(iv) It reacts with strong alkalies to form metaborates and hydrogen.

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$$

(v) It reacts with chlorine forming boron trichloride.

$$B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$$

(vi) In presence of anhydrous aluminium chloride, it reacts with dry HCl.

$$\begin{array}{c} B_2H_6 + HCl & \longrightarrow & B_2H_5Cl & + H_2 \\ & & \text{Chlorodiborane} \end{array}$$

(vii) Lithium borohydride is formed when diborane reacts with LiH in presence of ether.

$$2\text{LiH} + \text{B}_2\text{H}_6 \xrightarrow{\text{Ether}} 2\text{LiBH}_4$$

(viii) It reacts with carbon monoxide under pressure to form carbonyl, BH<sub>3</sub>CO.

$$B_2H_6 + 2CO \longrightarrow 2BH_3CO$$

(ix) It reacts with sodium amalgam forming an addition compound.

$$B_2H_6 + 2Na \text{ (amalgam)} \longrightarrow B_2H_6 \cdot Na_2$$

(x) At low temperatures, an addition product, B<sub>2</sub>H<sub>6</sub>·2NH<sub>3</sub>, is obtained with ammonia.

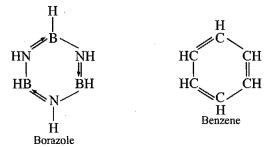
$$B_2H_6 + 2NH_3 \xrightarrow{\text{Low temp.}} B_2H_6 \cdot 2NH_3$$

When the addition product is heated at 200°C, a volatile compound borazole or inorganic benzene is formed.

$$3B_2H_6\cdot 2NH_3 \ \longrightarrow \ 2B_3N_3\cdot H_6 \ + \ 12H_2$$

Borazole

Borazole has a ring structure like benzene.

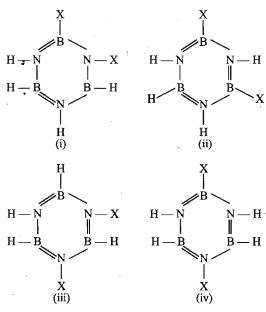


Note: (i) The addition product B<sub>2</sub>H<sub>6</sub>·2NH<sub>3</sub> is considered as an ionic product. It can be represented as [BH<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>†</sup>[BH<sub>4</sub>].

When diborane with excess of NH3 mixture is heated at high temperature, boron nitride (BN)<sub>x</sub> is formed.

$$B_2H_6 + NH_3 \xrightarrow{Excess of NH_3} (BN)_x$$
high temp. Boron nitride

- (iii) The  $\pi$  bond in borazole (borazine) is formed by back bonding involving filled p-orbital of N and vacant orbital of B. However, borazole is more reactive than benzene.
- (iv) Disubstituted borazole, B<sub>3</sub>N<sub>3</sub>H<sub>4</sub>X<sub>2</sub> can have four isomers while benzene can have three.



#### Uses

The important uses of diborane are:

- (i) as a catalyst in polymerisation reactions.
- (ii) as a reducing agent in organic reactions.
- (iii) for making high energy fuels and propellants.
- (iv) for preparing hydrocarbons, alcohols, ketones and acids through hydroboration method.

Structure: Diborane is an example of electron deficient **compound.** Boron atom has three half filled orbitals in excited state, i.e., it can link with three hydrogen atoms. Thus, while each boron atom in diborane can link to itself three hydrogen atoms, there are no electrons left to form a bond between two boron atoms as shown below:

Dilthey in 1921 proposed a bridge structure for diborane. Four hydrogen atoms, two on the left and two on the right, known as terminal hydrogens and two boron atoms lie in the same plane. Two hydrogen atoms forming bridges, one above and other below, lie in a plane perpendicular to the rest of molecule. This structure shows that there are two types of hydrogen atoms—Terminal and bridging. 4-terminal hydrogen

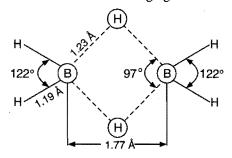


Fig. 8.3

atoms can easily be replaced by methyl groups but when two bridging hydrogen atoms are attacked, the molecule is ruptured.

According to molecular orbital theory, each of the two boron atoms is in  $sp^3$  hybrid state. Of the four hybrid orbitals, three have one electron each while the fourth is empty. Two of the four orbitals of each of the boron atom overlap with two terminal hydrogen atoms forming two normal B—H  $\sigma$ -bonds. One of the remaining hybrid orbital (either filled or empty) of one of the boron atoms, 1s-orbital of hydrogen atom (bridge atom) and one of hybrid orbitals of the other boron atom overlap to form a delocalised orbital covering the three nuclei with a pair of electrons. Such a bond is known as **three centre two electron bonds.** 

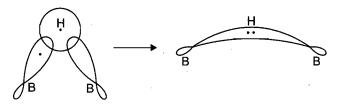


Fig. 8.4 Formation of three centre bond (B—H—B)

Similar overlapping occurs in one hydrogen atom (bridging) and fourth hybrid orbital of each boron atom. Thus, the formation of diborane molecule can be depicted as shown in the following figure:

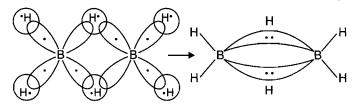


Fig. 8.5 Structure of diborane

On account of repulsion between the two hydrogen nuclei, the delocalised orbitals of bridges are drifted away from each other giving the shape of a banana. The three centre two electron bonds are also known as **banana bonds**.

#### 🍛 6. Boron Nitride, BN

#### **Preparation**

It is prepared:

(i) by heating boron in the atmosphere of nitrogen or ammonia.

$$2B + N_2 \longrightarrow 2BN$$
  
 $2B + 2NH_3 \longrightarrow 2BN + 3H_2$ 

(ii) by heating borax with ammonium chloride at red heat.

$$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2BN + 2NaCl + B_2O_3 + 4H_2O$$

The resulting mass is treated with dil. HCl, B<sub>2</sub>O<sub>3</sub> and NaCl dissolve and BN is left insoluble.

(iii) by heating B<sub>2</sub>O<sub>3</sub> with Hg(CN)<sub>2</sub>.

$$B_2O_3 + Hg(CN)_2 \longrightarrow 2BN + CO + CO_2 + Hg$$

(iv) Pure BN is obtained by the action of NH3 on BCl3.

$$\begin{array}{c} BCl_3 + 6NH_3 \longrightarrow B(NH_2)_3 + 3NH_4Cl \\ Boronamide \\ 2B(NH_2)_3 \xrightarrow{Heat} B_2(NH)_3 + 3NH_3 \\ Boronimide \end{array}$$

$$B_2(NH)_3 \longrightarrow 2BN + NH_3$$

Boron nitride is often prepared by chemical vapour deposition, a procedure used in the fabrication of several other ceramics as well. In this method, a controlled chemical reaction of gases on a contoured, heated surface gives a solid product of the desired shape. If a cup made of BN is needed a cup-shaped mold is heated to a temperature exceeding  $1000^{\circ}$ C, and a mixture of  $BCl_3(g)$  and  $NH_3(g)$  is passed over its surface the reaction,  $BCl_3(g) + NH_3(g) \longrightarrow BN(s) + 3HCl(g)$  deposits a cup-shaped layer of BN(s).

#### **Properties**

It is a white powder. It melts at very high temperature, 3000°C. It is insoluble in water. However, it gets decomposed when heated in steam under pressure to yield ammonia.

$$2BN + 3H_2O \longrightarrow B_2O_3 + 2NH_3$$

It is chemically inert compound. It remains unaffected by mineral acids. It dissolves in HF yielding ammonium borofluoride.

$$BN + 4HF \longrightarrow NH_4BF_4$$

It fails to react with alkalies. However, when fused with  $K_2CO_3$ , it yields potassium cyanate and potassium metaborate.

$$K_2CO_3 + BN \longrightarrow KCNO + KBO_2$$

**Structure:** The structure of boron nitride, BN, resembles to that of graphite (Fig. 9.3), consisting of flat planes of hexagons. In boron nitride, however, the hexagons consist of alternating B and N atoms in place of C atoms (Fig. 8.6).

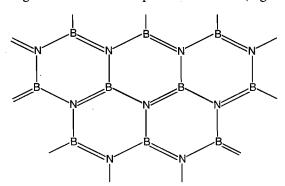


Fig. 8.6 The structure of boron nitride, BN

Recently, another crystalline form of boron nitride called **borazon** has been synthesised by application of high temperature and pressure. This form is even harder than diamond. It is used as abrasive.

Boron nitride cups and tubes are used to contain and evaporate molten metals. One form of boron nitride powder, BN, is composed of flat, platelike crystals that can easily slide over one another. It is used in cosmetics, where it gives a silky texture.

### 8.7 ALUMINIUM

**Occurrence:** Aluminium is a third most abundant element forming 8.3% of the earth's crust. It is a constituent of clay, slate and many types of silicate rocks. It is found only in the combined state. The important minerals are:

(i) Oxides: (a) Corundum (ruby, sapphire, emerald), Al<sub>2</sub>O<sub>3</sub>. (b) Diaspore, Al<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O. (c) Gibbsite, Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O. (d) Bauxite, Al<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O. It is the chief ore of aluminium from which extraction of aluminium is made. It is usually associated with varying amounts of ferric oxide and silica.

The pure aluminium oxide is colourless, but the presence of impurities can give various colours to it. Naturally occurring some impure forms of alumina, Al<sub>2</sub>O<sub>3</sub> are beautiful, rare and highly prized (a) Sapphire, alumina with Fe<sup>3+</sup> and Ti<sup>4+</sup> impurities (usually blue), (b) Ruby, alumina with Cr<sup>3+</sup> and (c) Topaz alumina with Fe<sup>3+</sup> impurities (usually red) are gem quality corundum.

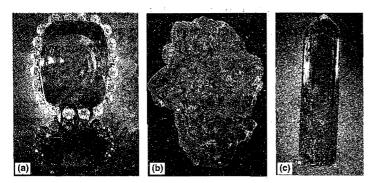


Fig. 8.7 Some of the impure forms of alumina (corundum) are prized as gems. (a) Sapphire is alumina with Fe<sup>3+</sup> and Ti<sup>4+</sup> impurities. (b) Ruby is alumina with Cr<sup>3+</sup> impurities.
 (c) Topaz is alumina with Fe<sup>3+</sup> impurities

- (ii) Fluoride: Cryolite, Na<sub>3</sub>AlF<sub>6</sub>. It is the second important ore of aluminium.
  - (iii) Basic sulphate: Alunite or alum stone,

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$$
.

- (iv) Basic phosphate: Turquoise, AlPO<sub>4</sub>·Al(OH)<sub>3</sub>·H<sub>2</sub>O. It is usually blue coloured due to presence of copper phosphate.
- (v) Silicates: Feldspar, KAlSi<sub>3</sub>O<sub>8</sub>, kaolin, porcelain, mica, china clay, slate, etc., Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O.

**Extraction:** Aluminium is mainly isolated from bauxite ore which is generally contaminated with ferric oxide and silica. The removal of ferric oxide and silica from bauxite ore is essential before it is subjected to electrolysis because it is rather difficult to remove iron and silicon from aluminium

metal, the presence of these elements makes the aluminium metal brittle and liable to corrosion. Thus, the extraction of aluminium from bauxite ore involves the following three steps.

- (i) Purification of bauxite ore, *i.e.*, removal of ferric oxide and silica.
  - (ii) Electrolytic reduction of Al<sub>2</sub>O<sub>3</sub>.
  - (iii) Electrolytic purification of aluminium.
- (i) Purification of bauxite ore: The following methods are used for purifying the bauxite ore.

### (A) Baeyer's Process

This process is mainly applied to bauxite ore containing ferric oxide as chief impurity. The colour of such ore is usually red and hence called red bauxite.

The powdered ore is first roasted at a low temperature as to convert any ferrous oxide, if present, into ferric oxide. It is then digested with a concentrated solution of sodium hydroxide (density 1.45 g mL<sup>-1</sup>) in an autoclave under pressure at 150°C for several hours. The aluminium oxide dissolves in caustic soda forming soluble sodium meta aluminate (NaAlO<sub>2</sub>) while ferric oxide and silica remain insoluble and settle down. These are removed by filtration.

$$Al_2O_3 \cdot 2H_2O + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2O$$
Sodium metaaluminate

(soluble)

The sodium metaaluminate solution is agitated with freshly precipitated Al(OH)<sub>3</sub> for 36 hours when sodium metaaluminate undergoes hydrolysis with the formation of Al(OH)<sub>3</sub> precipitate.

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3$$

The precipitate is washed and dried.

The solution of NaOH is concentrated and used again.

#### (B) Hall's Process

Bauxite is fused with sodium carbonate. Aluminium oxide,  $Al_2O_3$  combines with sodium carbonate forming sodium metaaluminate. The fused mass is extracted with water where  $Fe_2O_3$  and  $SiO_2$  remain as insoluble in the residue.

$$Al_2O_3 + Na_2CO_3 \longrightarrow 2NaAlO_2 + CO_2$$
Aluminium Sodium Sodium metaaluminate

The solution containing sodium metaaluminate is warmed to 50–60°C and carbon dioxide is circulated through it. Al(OH)<sub>3</sub> separates out as precipitate.

$$2NaAlO_2 + CO_2 + 3H_2O \longrightarrow 2Al(OH)_3 + Na_2CO_3$$

The precipitate is filtered, washed and dried.

The solution of Na<sub>2</sub>CO<sub>3</sub> is concentrated and used again.

### (C) Serpeck's Process

This process is used when silica is present in considerable amounts in bauxite ore. The ore is mixed with coke and heated

at 1800°C in presence of nitrogen, where AlN (aluminium nitride) is formed.

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$$

Silica is reduced to silicon which volatilises off at this temperature.

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

AlN is hydrolysed with water into aluminium hydroxide. This process has one distinct advantage that ammonia is obtained as a valuable by-product.

Calcination of aluminium hydroxide: The aluminium hydroxide precipitate obtained in the above process is calcined at 1500°C in a rotary kiln to obtain pure aluminium oxide, Al<sub>2</sub>O<sub>3</sub> (commercially reffered as *alumina*).

$$2Al(OH)_3 \xrightarrow{1500^{\circ}C} Al_2O_3 + 3H_2O$$

(ii) Electrolytic reduction of pure alumina: The electrolysis of pure alumina faces two difficulties: (i) Pure alumina is a bad conductor of electricity, (ii) The fusion temperature of pure alumina is about 2000°C and at this temperature when the electrolysis is carried of fused mass, the metal formed vaporises as the boiling point of aluminium is 1800°C.

The above difficulties are overcome by using a mixture containing alumina, cryolite (Na<sub>3</sub>AlF<sub>6</sub>) and fluorspar (CaF<sub>2</sub>) in the ratio of 20 : 40 : 20. The fusion temperature of this mixture is 900°C and it is a good conductor of electricity.

The electrolysis is carried out in an iron box lined inside with gas carbon which acts as cathode. The anode consists of carbon rods which remains dip in the fused mixture of the electrolyte from above. The fused electrolyte is covered with a layer of coke (Fig. 8.8).

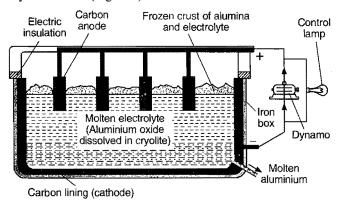


Fig. 8.8

The current passed through the cell serves two purposes—

- (i) Heating of the electrolyte—The temperature of the cell is automatically maintained at 900–950°C,
- (ii) Electrolysis—On passing current, aluminium is discharged at cathode. Aluminium being heavier than electrolyte sinks to the bottom and is tapped out periodically from tapping hole. Oxygen is liberated at anode. It attacks carbon rods forming CO and CO<sub>2</sub>. The process is continuous. When the

concentration of the electrolyte decreases, the resistance of the cell increases. This is indicated by the glowing of a lamp placed in parallel. At this stage more of alumina is added.

The exact mechanism of the electrolysis is not yet known. Two concepts have been proposed.

**First concept:** AlF<sub>3</sub> from cryolite ionises as,

$$AlF_3 \iff Al^{3+} + 3F^{-}$$

Al<sup>3+</sup> ions are discharged at cathode and F<sup>-</sup> ions at anode.

$$Al^{3+} + 3e \longrightarrow Al$$
 (at cathode)  
 $2F^{-} \longrightarrow F_2 + 2e$  (at anode)

The liberated fluorine reacts with alumina to form  $AlF_3$  and  $O_2$ . The oxygen attacks the carbon anodes to form CO and  $CO_2$ .

$$Al_2O_3 + 3F_2 \longrightarrow 2AlF_3 + \frac{3}{2}O_2$$

$$2C + O_2 \longrightarrow 2CO$$

$$C + O_2 \longrightarrow CO_2$$

Anodes are replaced frequently.

Second concept: Alumina (Al<sub>2</sub>O<sub>3</sub>) ionises as,

$$Al_2O_3 \Longrightarrow Al^{3+} + AlO_3^{3+}$$
Cathode Anode
 $Al^{3+} + 3e \longrightarrow Al \text{ (at cathode)}$ 

At anode AlO<sub>3</sub> is oxidised.

$$4AlO_3^{3-} \longrightarrow 2Al_2O_3 + 3O_2 + 12e$$
 (at anode)

Thus, the overall chemical reaction taking place during electrolysis is,

$$2Al_2O_3 \longrightarrow 4Al + 3O_2$$

Aluminium of 99.8% purity is obtained from this process.

(iii) Refining of aluminium by Hoope's electrolytic method: Aluminium is further purified by Hoope's process. The electrolytic cell consists of an iron box lined inside with carbon. The cell consists of three layers which differ in specific gravities. The upper layer is of pure aluminium which acts as cathode. The middle layer consists of a mixture of the fluorides of Al, Ba and Na. The lowest layer consists of impure aluminium which acts as anode. The middle layer works as electrolyte.

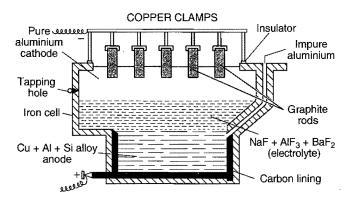


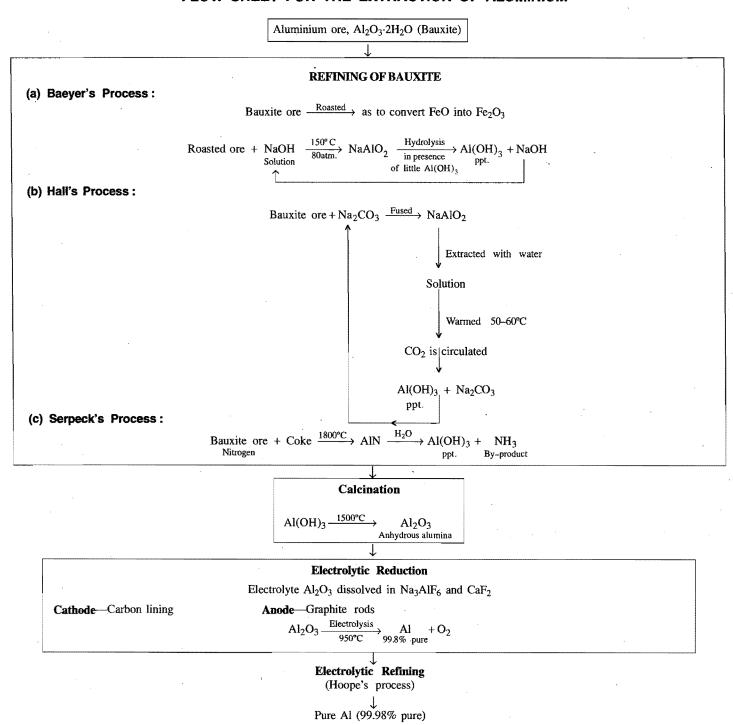
Fig. 8.9

The graphite rods dipped in pure aluminium and Cu-Al alloy rod at the bottom in the impure aluminium work as conductors. On electrolysis, aluminium is deposited at cathode from the middle layer and an equivalent amount of aluminium is taken up by the middle layer from the bottom layer (impure aluminium). Therefore, aluminium is transferred from bottom to the top layer through middle layer while the impurities are left behind. Aluminium thus obtained is 99.98% pure.

#### **Physical Properties**

(a) Aluminium is a bluish white lustre metal. The lustre is destroyed on long exposure to air due to formation of a thin film of oxide on the surface. (b) The density of aluminium is 2.7 g mL<sup>-1</sup> (light metal). It is malleable and ductile. (c) It is a good conductor of heat and electricity. (d) It melts at 660°C and boils at 1800°C. (e) It can be welded and cast but difficult to solder.

#### FLOW SHEET FOR THE EXTRACTION OF ALUMINIUM



### **Chemical Properties**

Aluminium is a chemically reactive metal although much less reactive than the alkali metals or alkaline earth metals.

(a) Action of air: Aluminium is not affected by dry air but in moist air a thin film of oxide is formed over its surface. Which protects the underlying metal from further reaction. It burns in oxygen producing brilliant light. The metal will burn vigorously once started however.

$$4A1 + 3O_2 \longrightarrow 2Al_2O_3$$

The reaction is highly exothermic and the heat evolved is used in the thermite process for the reduction of oxides of Cr, Fe, Mn, etc.

(b) Action of water: Pure aluminium is not affected by pure water. The impure aluminium is readily corroded by water containing salts (sea water). Aluminium decomposes boiling water evolving hydrogen.

$$2Al + 6H2O \longrightarrow 2Al(OH)3 + 3H2\uparrow$$

(c) Action of acids: The oxidation potential of aluminium is 1.66 volts. Thus, it is strongly electropositive, very reactive and a powerful reducing agent. It dissolves in HCl (dil. and conc.) and dilute sulphuric acid, evolving hydrogen.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2 \uparrow$$
  
 $2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2 \uparrow$ 

The reaction with dil. H<sub>2</sub>SO<sub>4</sub> is very slow probably on account of the insolubility of the oxide film in this acid.

Hot concentrated sulphuric acid dissolves Al with evolution of SO<sub>2</sub>.

$$2AI + 6H2SO4 \longrightarrow AI2(SO4)3 + 3SO2 + 6H2O$$

Dilute and concentrated HNO<sub>3</sub> has no effect on Al, *i.e.*, Al is rendered passive by nitric acid. This is due to surface oxidation and formation of a thin film of oxide on its surface. Organic acids have little action on Al at ordinary temperatures.

(d) Action of alkalies: Aluminium is attacked by caustic alkalies with the evolution of hydrogen.

$$2Al + \underbrace{2NaOH + 2H_2O}_{Solution} \longrightarrow \underbrace{2NaAlO_2}_{Sodium meta-aluminate (soluble)} + 3H_2 \uparrow$$

$$2Al + 6NaOH \longrightarrow \underbrace{2Na_3AlO_3}_{Solution} + 3H_2 \uparrow$$

(e) Action of non-metals: Besides oxygen, aluminium reacts with non-metals directly to form corresponding compounds. Aluminium when heated in the atmosphere of

nitrogen, forms aluminium nitride.

$$2A1 + N_2 \longrightarrow 2AIN$$

Aluminium powder when fused with sulphur forms aluminium sulphide.

$$2A1 + 3S \longrightarrow Al_2S_3$$

Finely powdered heated aluminium combines with halogens to form corresponding halides.

$$2Al + 3X_2 \longrightarrow 2AlX_3$$
$$(X_2 = F_2, Cl_2, Br_2, I_2)$$

All these compounds are hydrolysed with water.

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$
  
 $Al_2S_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2S$   
 $AlX_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HX$ 

(f) Reducing agent: It is a good reducing agent and reduces oxides of metals like Cr, Fe, Mn, etc.

$$Cr_2O_3 + 2AI \longrightarrow 2Cr + Al_2O_3 + heat$$
  
 $Fe_2O_3 + 2AI \longrightarrow 2Fe + Al_2O_3 + heat$   
 $3Mn_3O_4 + 8AI \longrightarrow 9Mn + 4Al_2O_3 + heat$ 

It reduces oxides of non-metals also.

$$3\text{CO}_2 + 4\text{Al} \longrightarrow 2\text{Al}_2\text{O}_3 + 3\text{C}$$
  
 $3\text{SiO}_2 + 4\text{Al} \longrightarrow 2\text{Al}_2\text{O}_3 + 3\text{Si}$ 

(g) Displacement of other metals: Being more electropositive it displaces copper, zinc and lead from the solutions of their salts.

$$3ZnSO_4 + 2Al \longrightarrow Al_2(SO_4)_3 + 3Zn$$
  
 $3CuSO_4 + 2Al \longrightarrow Al_2(SO_4)_3 + 3Cu$ 

#### **Uses**

- (i) Aluminium being cheap and light metal is largely used for making household utensils, trays, frames, etc. Bodies of automobiles, aircraft and roofing are made of aluminium sheet.
- (ii) Thin foils of Al are used in wrapping soaps, cigarettes and confectionary.
- (iii) Al wire is used in transmission lines and coils for dynamos and motors.
- (iv) It is used for making silvery paints for covering iron and other materials.
- (v) It is used in thermite process for the extraction of Cr, Mn, etc.
- (vi) Since it is not attacked by nitric acid, it is used in chemical plants and for transporting nitric acid.
- (vii) Because of its lightness, good conductivity and resistance to corrosion, it is used for making alloys which find applications in industries and arts. The important alloys of aluminium are:

Name of the alloy	Approximate composition	Uses
1. Magnalium	95% Al, 5% Mg	In the construction of airships, balances and pistons of motor engines.
2. Duralumin	95% Al, 4% Cu, 0.5% Mg, 0.5% Mn	Aeroplanes and automobile parts as its strength of toughness is comparable to mild
		steels.
3. Aluminium bronze	90% Cu, 9.5% Al, 0.5% Sn	For making utensils, cheap artificial jewellery, photo frames, coins, golden paints.
4. Nickeloy	95% Al, 4% Cu, 1% Ni	Aircraft parts.
5. Y-alloy	93% Al, 4% Cu, 2% Ni, 1% Mg	For making pistons and machinery parts.
6. Alnico	77% Steel; 2% Ni, 20% Al, 1% Co	For making permanent magnets.

- (viii) Aluminium amalgam is used as a reducing agent.
- (ix) Aluminium powder is used in fire works, flash light powder and in thermite welding.

## 8.8 COMPOUNDS OF ALUMINIUM

### 1. Aluminium Oxide or Alumina, Al<sub>2</sub>O<sub>3</sub>

It occurs in nature as colourless corundum and tinted with metallic oxides as ruby (red), sapphire (blue), amethyst (violet), emery (green), etc. These coloured oxides are precious stones. Hydrated oxide (Al<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O) occurs as bauxite.

It is prepared by igniting aluminium hydroxide, aluminium sulphate or ammonium alum.

$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

$$Al_2(SO_4)_3 \longrightarrow Al_2O_3 + 3SO_3$$

$$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \longrightarrow$$

$$Al_2O_3 + 2NH_3 + 4SO_3 + 25H_2O$$

It is obtained in crystalline form by strongly heating a mixture of aluminium fluoride and boric oxide.

$$2AlF_3 + B_2O_3 \longrightarrow Al_2O_3 + 2BF_3$$

**Properties:** It is a white solid, insoluble in water. It is a stable and unreactive substance. It begins to volatilise at 1750°C and melts at 2050°C. It boils at 2250°C.

It shows amphoteric nature. When it is fused with oxides of chromium, iron and cobalt, synthetic semi-precious stones are obtained.

**Uses:** It is widely used for making bauxite bricks which are used for lining furnaces. Fused alumina is used as refractory material. When heated in an electric arc at 3000°C, a hard powder known as **alundun** is obtained which is used as abrasive. With lime, it is used as bauxite cement which is not affected by sea water. It is used in chromatography, in extraction of aluminium and in preparing precious stones.

### 2. Aluminium Chloride, AICl<sub>3</sub>

(i) Anhydrous aluminium chloride: It is prepared by passing dry HCl gas or chlorine gas over heated aluminium

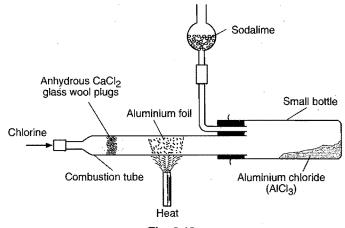


Fig. 8.10

turnings in absence of air. The vapours of aluminium chloride are condensed when solid anhydrous aluminium chloride is obtained.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$
  
 $2Al + 3Cl_2 \longrightarrow 2AlCl_3$ 

It can also be obtained by heating a mixture of alumina and carbon in an atmosphere of chlorine.

Al<sub>2</sub>O<sub>3</sub> + 3C + 3Cl<sub>2</sub> 
$$\xrightarrow{1000^{\circ}\text{C}}$$
 2AlCl<sub>3</sub> + 3CO

Vapours

↓ Cooled

Solid anhydrous
aluminium chloride

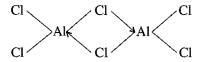
(ii) Hydrated aluminium chloride: AlCl<sub>3</sub>·6H<sub>2</sub>O, is formed when aluminium metal or aluminium hydroxide is dissolved in dilute hydrochloric acid.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$
  
 $Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$ 

HCl gas is circulated through the solution to obtain crystals of hydrated aluminium chloride.

#### **Properties**

(a) Anhydrous aluminium chloride is a white solid. It is deliquescent and fumes in air. On heating it sublimes at 180°C and the vapour density corresponds to the formula Al<sub>2</sub>Cl<sub>6</sub>. It is covalent when anhydrous as it does not conduct current in fused state. It is soluble in organic solvents such as alcohol, ether, benzene, etc. The dimeric formula is retained in nonpolar solvents but is broken into [Al(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> on dissolution in water on account of high heat of hydration. The molecule (dimer) is an autocomplex and is represented as,



(b) Anhydrous aluminium chloride fumes in moist air due to evolution of HCl.

$$Al_2Cl_6 + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl$$

When dissolved in water, it changes into hydrated aluminium chloride which is ionic in nature.

$$Al_2Cl_6 + 12H_2O \longrightarrow 2AlCl_3 \cdot 6H_2O$$
  
 $AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^{-}$ 

(c) Anhydrous aluminium chloride forms an addition product with ammonia gas.

$$Al_2Cl_6 + 12NH_3 \longrightarrow 2[AlCl_3 \cdot 6NH_3]$$

(d) The solution of aluminium chloride in water is acidic in nature due to hydrolysis.

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$
Weak base Strong acid

(e) When ammonium hydroxide is added to the solution of aluminium chloride, a gelatinous precipitate of aluminium hydroxide appears which does not dissolve in excess of NH<sub>4</sub>OH.

$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3 + 3NH_4Cl$$

(f) When sodium hydroxide is added to the solution of aluminium chloride drop by drop, a white gelatinous precipitate appears which dissolves in excess of sodium hydroxide forming sodium meta-aluminate.

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$$
  
 $Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$ 

#### Uses

- (i) It is used as a catalyst in Friedel-Craft's reaction.
- (ii) It is also used in the manufacture of gasoline by cracking of high boiling fractions of petroleum.
- (iii) It finds extensive use in the manufacture of dyes, drugs and perfumes.

#### 3. Alums

Formerly, the term alum was used to describe only one double sulphate with 24 molecules of water of crystallisation, potassium aluminium sulphate,  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ , but now this term is used for all the double sulphates having the composition,

$$M_2SO_4 \cdot M_2'(SO_4)_3 \cdot 24H_2O$$

where M stands for monovalent basic radicals such as Na<sup>+</sup>, Kb<sup>+</sup>, Cs<sup>+</sup>, Ag<sup>+</sup>, Tl<sup>+</sup>, NH<sub>4</sub> and M' for trivalent basic radicals such as Al<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Mn<sup>3+</sup>, Co<sup>3+</sup>, etc.

Some examples of alums are:

Potash alum	$K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$
(commonly called alum)	
Ammonium alum	$(NH_4)_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$
Sodium alum	$Na_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$
Chrome alum	$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$
Ferric alum	$(NH_4)_2SO_4\cdot Fe_2(SO_4)_3\cdot 24H_2O$

Alums are generally obtained when hot solutions of equimolar quantities of their constituent sulphates are mixed and the resulting solution is subjected to crystallisation.

Alums are crystalline compounds. In alums each metal ion is surrounded by six water molecules and the crystals of alums consist of  $[M(H_2O)_6]^+$ ,  $[M'(H_2O)_6]^{3+}$  and  $SO_4^{2-}$  ions. Alums are fairly soluble in hot water but less soluble in cold water. The solutions are acidic and have stringent taste. The solutions show the properties of ions of the constituent salts. The alums are isomorphous to each other and form mixed crystals.

Each alum has different melting point. Alums lose water of crystallisation when heated. If rapidly heated to a high temperature, the alum swells up and a porous mass called **burnt alum** is left behind.

### Potash Alum, K2SO4·Al2(SO4)3·24H2O

It is commonly known as alum.

#### Preparation

(i) From bauxite or aluminium sulphate: Bauxite is boiled with sulphuric acid to form aluminium sulphate. To this solution calculated quantity of  $K_2SO_4$  is added. The solution is concentrated and cooled. After some time crystals of potash alum are obtained.

$$\begin{array}{c} Al_2O_3 \,+\, 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 \,+\, 3H_2O \\ Al_2(SO_4)_3 \,+\, K_2SO_4 \,+\, 24H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \\ & \quad \quad \text{Potash alum} \end{array}$$

(ii) From alum stone or alunite: Alum stone is treated with dilute sulphuric acid and the solution is boiled. A calculated quantity of  $K_2SO_4$  is added to the solution. The solution on cooling yields crystals of potash.

### **Properties**

- (a) It is a white crystalline compound.
- (b) It is soluble in water and its aqueous solution is acidic due to hydrolysis of  $Al_2(SO_4)_3$ .
- (c) On heating it swells up on account of elimination of water molecules.

$$\begin{array}{c} K_2 SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \xrightarrow{200^{\circ}C} K_2 SO_4 \cdot Al_2(SO_4)_3 \, + \, 24H_2O \\ K_2 SO_4 \cdot Al_2(SO_4)_3 \xrightarrow{Red \ hot} K_2 SO_4 \, + \, Al_2O_3 \, + \, 3SO_3 \end{array}$$

(d) Its aqueous solution contains  $K^+$ ,  $Al^{3+}$  and  $SO_4^{2-}$  ions and their usual tests can be performed.

#### Uses

It is used:

- (i) as a mordant\* in dyeing and calico printing.
- (ii) in sizing of cheap quality of paper.
- (iii) in purification of water.
- (iv) as antiseptic and in stopping bleeding from cuts.
- (v) in leather tanning.

#### 4. Ultramarine

It is an artificial **Lapis-Lazuli**. Lapis-Lazuli is a rare mineral which has fine blue colour. It is a complex silicate of sodium

Kras 3 - Usa

The alums are effective in precipitating colloids, *i.e.*, act as coagulants. The alums have germicide properties. Alums are thus used in the purification of water, tanning of leather, as mordants in dyeing and as antiseptics.

<sup>\*</sup> A "mordant" is a compound that helps to attach the dye to the fabric.

and aluminium containing about 12 per cent of sulphur probably in the form of sodium sulphide.

It can be prepared artificially by heating a mixture of kaolin, soda ash, sulphur and charcoal to bright red heat. At first a white mass is formed which changes to a green mass in air. It is powdered and heated with more of sulphur where the blue variety having the composition Na<sub>5</sub>Al<sub>3</sub>Si<sub>3</sub>S<sub>3</sub>O<sub>12</sub> is obtained. Blue variety on heating in a current of dry chlorine changes to violet variety.

However, the blue variety is most common. It is used:

- (i) in making blue paint.
- (ii) in laundry for blueing purposes.
- (iii) in making wall paper and blue tinted paper.
- (iv) in calico-printing.

# 8.9 GOLDSCHMIDT'S ALUMINO-THERMIC PROCESS

Aluminium has the power of displacing elements less electropositive than itself from their oxides as it has great affinity for oxygen at high temperatures. The reaction being so strongly exothermic that the metal set free is obtained in the molten condition and it is protected from oxidation by a layer of fluid slag consisting of Al<sub>2</sub>O<sub>3</sub>.

Oxide + Al 
$$\longrightarrow \underbrace{Al_2O_3 + metal}_{Molton state}$$
 + heat energy

The reaction forms the basis of the alumino-thermic process. It was discovered by **Goldschmidt.** The process has two main applications:

(i) Extraction of metals and non-metals: The metals like Cr, Mo, Mn and non-metals like boron, silicon, etc., can be extracted from their corresponding oxides.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3 + heat energy$$
  
 $3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3 + heat energy$   
 $B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3 + heat energy$   
 $3SiO_2 + 4Al \longrightarrow 3Si + 2Al_2O_3 + heat energy$ 

The oxide is mixed with aluminium powder. The mixture is ignited in a fire clay crucible surrounded by sand with the help of a cartridge (containing magnesium powder and barium

peroxide). The large amount of heat generated in the reaction fuses both the alumina and the element set free. Two distinct layers are formed which are removed easily.

(ii) Thermite welding of metals: Another application is the welding of metals especially the welding of steel. The broken part to be welded is surrounded by a mould of sand and clay and heated to redness by means of a gasoline torch or a blast lamp. A mixture of aluminium powder and  $Fe_2O_3$  in the ratio of 1:3 (known as thermite) is taken in a crucible lined with magnesite and having a plug hole (Fig. 8.11). This is covered with a mixture of magnesium powder and barium peroxide with a magnesium ribbon inserted into it. The thermite is ignited with magnesium ribbon. Iron oxide is reduced to iron

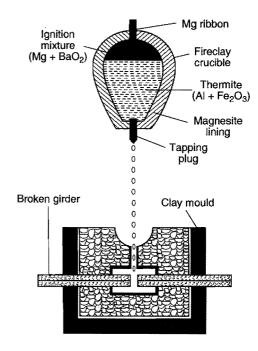


Fig. 8.11 Thermite welding

and temperature rises to about 2500°C. Molten iron thus produced is tapped into the parts to be welded. The heated surface of the broken iron melts and mingles with the molten iron, thus giving a perfect weld.

## SOME SOLVED PROBLEMS

**Example 1.** Starting from boric acid how would you prepare?

(a) Boric anhydride, (b) Boron trichloride, (c) Boron trifluoride, (d) Boron hydrides, (e) Ethyl borate, (f) Meta and tetraboric acids.

#### **Solution:**

(a) Boric acid on strong heating forms boric anhydride.  $2H_3BO_3 \xrightarrow{\text{Red hot}} B_2O_3 + 3H_2O$  (b) Boric acid is first converted into boric anhydride. It is now mixed with carbon and the mixture is heated in a current of chlorine when boron trichloride is formed.

$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$$

(c) It is prepared by heating boric acid with CaF<sub>2</sub> and concentrated sulphuric acid.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2F_2$$

$$2H_3BO_3 + 3H_2F_2 \longrightarrow 2BF_3 + 6H_2O$$

(d) Boric acid is first converted into boric anhydride. It is then heated with excess of magnesium powder in a covered crucible. The magnesium boride so formed is treated with dilute HCl when a mixture of boron hydrides is obtained.

$$H_3BO_3 \xrightarrow{\text{Red hot}} B_2O_3 \xrightarrow{\text{Mg}} Mg_3B_2 \xrightarrow{\text{Dil. HCl}}$$

A mixt. of boron hydrides

(e) Ethyl borate is formed when the mixture of boric acid and ethyl alcohol is warmed with concentrated sulphuric acid in the form of vapours.

$$3C_2H_5OH + H_3BO_3 \longrightarrow (C_2H_5)_3BO_3 + 3H_2O_3$$

(f) Orthoboric acid when heated at 100°C, decomposes into metaboric acid.

$$H_3BO_3 \xrightarrow{100^{\circ}C} HBO_2 + H_2O$$

When heated at 160°C, it decomposes into tetraboric acid.

or 
$$4H_3BO_3 \xrightarrow{160^{\circ}C} H_2B_4O_7 + 5H_2O$$
$$4HBO_2 \longrightarrow H_2B_4O_7 + H_2O$$

**Example 2.** Identify (A) and (B) in the following reactions:

Colemanite + (A) 
$$\longrightarrow Na_2B_4O_7$$
  
 $Na_2B_4O_7 + (B) \longrightarrow H_3BO_3$ 

#### **Solution:**

(A) is sodium carbonate.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3$$

(B) is either concentrated H<sub>2</sub>SO<sub>4</sub> or HCl.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$
  
 $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$ 

**Example 3.** Explain the following with appropriate reason:

- (i) Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water. [I.I.T. 1994]
- (ii) In the electrolytic manufacture of aluminium, carbon anodes are consumed.
- (iii) Cryolite is added to alumina in the electrolytic manufacture of aluminium.
  - (iv) Anhydrous AlCl<sub>3</sub> fumes in air.
  - (v) Alum is used in settling muddy water.

#### Solution:

- (i) The thin protective film of oxide, Al<sub>2</sub>O<sub>3</sub>, is formed which protects the metal from further attack of air and water and thus, it is stable in air and water.
- (ii) During electrolysis of cryolite and alumina in the manufacture of aluminium, oxygen is evolved at anode.

$$2F \longrightarrow F_2 + 2e$$
 (at anode);  $Al_2O_3 + 3F_2 \longrightarrow 2AlF_3 + \frac{3}{2}O_2$ 

Oxygen reacts with carbon anodes forming CO and CO<sub>2</sub>. Thus, carbon anodes are consumed.

- (iii) Pure alumina has very high fusion temperature and is bad conductor of electricity. To reduce its fusion temperature and to make it as good conductor of electricity, cryolite is added.
- (iv) Anhydrous aluminium chloride is hydrolysed in moist air and fumes of HCl are given out.

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$

(v) Alum acts as a germicide and strong coagulant. The muddy water consists colloidal particles of negative charge which are coagulated by Al<sup>3+</sup> ions given by alum. The coagulated mass then settles down.

**Example 4.** An inorganic Lewis acid (X) shows the following reactions:

- (i) It fumes in moist air.
- (ii) The intensity of fumes increases when a rod dipped in  $NH_4OH$  is brought near to it.
- (iii) An acidic solution of (X) on addition of  $NH_4Cl$  and  $NH_4OH$  gives a precipitate which dissolves in NaOH solution.
- (iv) An acidic solution of (X) does not give a precipitate with  $H_2S$ .

Identify (X) and give chemical reactions at steps (i) to (iii).

[Roorkee 1994]

#### Solution:

X is a Lewis acid and fumes in air, it may be anhydrous AlCl<sub>3</sub>.

(i) 
$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$
  
Fumes

The fumes intensify as HCl and NH<sub>4</sub>OH react to form NH<sub>4</sub>Cl.

- (ii)  $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$
- (iii) Al(OH)<sub>3</sub> is precipitated on addition of NH<sub>4</sub>Cl and NH<sub>4</sub>OH.

This dissolves in NaOH forming sodium meta-aluminate—

$$AlCl3 + 3NH4OH \longrightarrow Al(OH)3 + 3NH4Cl$$

$$ppt.$$

$$Al(OH)3 + NaOH \longrightarrow NaAlO2 + 2H2O$$
Soluble

No precipitate is formed by passing H<sub>2</sub>S through solution.

**Example 5.** Explain the following:

- (i) Boron and aluminium halides behave as Lewis acids.
- (ii) Boron tribromide is stronger acid than boron trifluoride.
- (iii) Aluminium forms  $[AlF_6]^{3-}$  ion but boron does not form  $[BF_6]^{3-}$  ion.
  - (iv) Boron has high melting and boiling points.
- (v) The  $p\pi$ — $p\pi$  back bonding occurs in the halides of boron and not in those of aluminium.

#### **Solution:**

(i) Both boron and aluminium atoms in their halides  $(MX_3)$  possess six electrons in their valency shell. To complete octet,

they can accept a lone pair of electrons from a donor and thus act as Lewis acids.

- (ii) Back bonding occurs in boron halides to compensate the electron deficiency and hence Lewis acidity is decreased. The tendency of back bonding is maximum in BF<sub>3</sub> and decreases from BF<sub>3</sub> to BI<sub>3</sub> as the size of the halogen increases. *p*-orbitals of high energy shells in bromine overlap less effectively with vacant *p*-orbital of boron in BBr<sub>3</sub>. Thus, BBr<sub>3</sub> is stronger acid than BF<sub>3</sub> as it has still tendency to accept electrons to remove electron deficiency.
- (iii) Maximum coordination number of boron is four as it does not have d-orbitals while the maximum coordination number of aluminium is 6. Thus, Al forms  $[AlF_6]^{3-}$  ion while boron does not form  $[BF_6]^{3-}$  ion.
- (iv) Boron has giant covalent polymeric structure both in solid and liquid states and thus, it has high melting and boiling points.
- (v) The tendency to show  $p\pi p\pi$  back bonding depends on the size of central atom. This tendency decreases as the size of the central atom increases. Since aluminium has larger size than boron, the back bonding is not possible.

**Example 6.** (i) A white precipitate (B) is formed when a mineral (A) is boiled with  $Na_2CO_3$  solution.

- (ii) The precipitate is filtered and the filtrate contains two compounds (C) and (D). The compound (C) is removed by crystallisation and when  $CO_2$  is passed through the mother liquor left, (D) changes to (C).
- (iii) The compound (C) on strong heating gives two compounds (D) and (E).
- (iv) (E) on heating with cobalt oxide produces blue coloured substance (F).

Identify (A) to (F) and give chemical reactions for the reactions at steps (i) to (iv). [Roorkee 1995]

#### **Solution:**

(i) The mineral (A) is colemanite, Ca<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·5H<sub>2</sub>O.

$$\begin{array}{c} \text{Ca}_2\text{B}_6\text{O}_{11} + 2\text{Na}_2\text{CO}_3(\textit{aq.}) \xrightarrow{\text{Boiled}} \\ (A) & 2\text{Ca}\text{CO}_3 + \underset{(B)}{\text{Na}_2\text{B}_4\text{O}_7} + 2\text{Na}\text{BO}_2 \\ & (B) & (C) & (D) \\ \hline \text{Insoluble} & \text{Soluble} \end{array}$$

(ii) (C), the borax is crystallised. The mother liquor consisting sodium metaborate is treated with  $CO_2$ .

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

$$(D) \qquad (C)$$

$$(iii) Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\text{Heated}} Na_2B_4O_7 + 10H_2O$$

$$Anhydrous$$

$$Na_2B_4O_7 \xrightarrow{\text{Strongly}} 2NaBO_2 + B_2O_3$$

$$(D) \qquad (E)$$

$$(iv) CoO + B_2O_3 \xrightarrow{\text{Heat}} Co(BO_2)_2 \qquad 1$$

$$Cobalt metaborate$$

$$Blue coloured$$

So,  $A = \text{Ca}_2\text{B}_6\text{O}_{11}$ ·SH<sub>2</sub>O Colemanite and  $F = \text{Co}(\text{BO}_2)_2$ ;  $B = \text{Ca}_3$ ;  $C = \text{Na}_2\text{B}_4\text{O}_7$ ·10H<sub>2</sub>O;  $D = \text{Na}_3\text{BO}_2$ ;  $E = \text{B}_2\text{O}_3$ .

**Example 7.** Al $F_3$  is insoluble in anhydrous HF but dissolves on addition of NaF. Al $F_3$  precipitates out of the resulting solution when gaseous BF<sub>3</sub> is bubbled through. Give reasons.

#### **Solution:**

Anhydrous HF is a covalent compound and is strongly H-bonded. Therefore, it does not furnish  $F^-$  ions and  $AlF_3$  does not react to form  $\left[AlF_6\right]^{3-}$  and remains undissolved. When NaF is added,  $F^-$  ions are furnished as NaF is an ionic compound.  $AlF_3$  with  $F^-$  ions forms a complex ion, the sodium salt of which is soluble.

$$3NaF + AlF_3 \longrightarrow Na_3[AlF_6]$$
Soluble complex

B, being smaller in size and having higher electronegativity, has much higher tendency to form complexes than Al. Therefore, when BF<sub>3</sub> is added to the Al-complex, AlF<sub>3</sub> gets precipitated and B-complex comes into existence.

$$Na_3AlF_6 + 3BF_3 \longrightarrow 3Na[BF_4] + AlF_3$$

#### **Example 8.** Give reasons:

- (i) A mixture of NaOH and aluminium pieces is used to open the drain.
  - (ii) Aluminium utensils should not be kept in water overnight.
  - (iii) Aluminium wire is used in transmission cables.
  - (iv) Aluminium alloys are used to make aircraft body. **Solution:**
- (i) NaOH reacts with Al and evolves hydrogen. The pressure of the evolved hydrogen can be used to open the clogged drains.
- (ii) Aluminium is slowly attacked by water and dissolved oxygen to form  $Al_2O_3$  on the surface. A very small amount of  $Al_2O_3$  may dissolve to give  $Al^{3+}$  ions. Since,  $Al^{3+}$  ions are injurious to health, the drinking water is not kept in aluminium utensils for long.
- (iii) Al is a good conductor of electricity and also not affected by atmosphere. Hence, it is used in transmission cables.
- (iv) Al-alloys are light, tough and corrosion resistant. Hence, Al-alloys are used for making aircraft bodies.

**Example 9.** What is inorganic benzene? Why it is so called? How will you get it from diborane? [West Bengal, J.E.E. 2005]

#### Solution:

Borazine or borazole (B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>) is known as inorganic benzene. It is so called because its structure is similar to that of benzene.

Like carbon in benzene, both B and N in borazine are  $sp^2$  hybridized. The  $\pi$ -bonding in borazine is dative, *i.e.*, a pair of electrons is donated by nitrogen to p-orbital of B.

At low temperature, borazine reacts with ammonia to form an addition compound.

$$B_2H_6 + 2NH_3 \longrightarrow B_2H_6 \cdot 2NH_3$$

When this compound is heated at 200°C, it decomposes to form borazine (volatile).

$$3B_2H_6 \cdot 2NH_3 \longrightarrow 2B_3N_3H_6 + 12H_2$$

**Example 10.** The first ionisation enthalpy of group 13 elements are:

Element	$\boldsymbol{B}$	Al	Ga	In	Tl
Ist I.E. $(kJ \ mol^{-1})$	801	577	579	558	589
How will you expla	in this	deviation.	from the	general	trend

#### Solution:

From B to Al, the ionisation enthalpy decreases as expected due to an increase in atomic size and screening effect. However, I.E. of Ga is only slightly higher than that of Al while that of thallium is much higher than those of Al, Ga and In. These deviations are explained as follows:

In periodic table, the position of Al, Ga, In and Tl in the respective periods is:

3rd period	Mg (s-block element)	Al
4th period	Zn (d-block element)	Ga
5th period	Cd (d-block element)	In
6th period	Hg (d-block element)	Tl

Thus, Al follows just after s-block elements while Ga and In follow after d-block elements and Tl after d- and f-block elements. The d-electrons in Ga and In and d- and f-electrons

in Tl do not shield the outer shell electrons very effectively. On account of this, the outer shell electrons are tightly held by the nucleus and hence higher energy is required for their removal. This explains why Ga has higher I.E. than Al. From Ga to In the shielding effect of additional 4d-electrons is slightly more than the effect of increased nuclear charge and hence, the I.E. of In is slightly less than Ga. In Tl, the shielding effect of d- and f-electrons is less than the effect of increased nuclear charge and hence, the I.E. is higher than In.

**Example 11.** Standard electrode potential values,  $E^o$  for  $Al^{3+}/Al$  is -1.66 V and that of  $Tl^{3+}/Tl$  is +1.26 V. Predict about the formation of  $M^{3+}$  ion in solution and compare the electropositive character of two metals.

#### **Solution:**

Standard electrode potential values suggest that aluminium has high tendency to make Al<sup>3+</sup> ions whereas Tl<sup>3+</sup> is unstable as it shows strong oxidising nature. Aluminium being able to form +3 ions easily, it is more electropositive than Tl.

**Example 12.** Account for the fact that aluminium chloride exists as a dimer,  $Al_2Cl_6$ .

#### Solution:

In AlCl<sub>3</sub>, Al is electron deficient (six electrons around Al) and chlorine atoms have lone pairs of electrons which can be donated. Al metal atoms complete their octet by forming a coordinate bond with chlorine atom of the other molecule, AlCl<sub>3</sub>. Thus, coordinate bond forming bridges by chlorine atoms between two Al atoms make a dimer molecule.

# SUMMARY AND IMPORTANT POINTS TO REMEMBER



- 1. Group IIIA or 13 of the periodic table consists of six elements-boron, aluminium, gallium, indium, thallium and ununtrium. These are p-block elements. The configuration of the outermost energy shell is  $ns^2np^1$ , i.e., this group marks the beginning of p-block.
- The members of group IIIA or 13 are less metallic in comparison to elements of IA (alkali metals) and IIA (alkaline earth metals) group.
  - Boron is regarded as a semi-metal. It is closer to non-metals than metals in its properties. Aluminium and rest of the elements are metallic in nature.
- 3. Aluminium is the most abundant metal and third most abundant element after oxygen and silicon by mass in the earth's crust. Boron is fairly rare but occurs as concentrated deposits of borax. Gallium is twice as abundant as boron but indium and thallium are much less common.
- 4. The atomic radii of members of group 13 are smaller than that of corresponding group IIA elements. The observed radius

- of Ga is nearly equal to that of Al. It is because the d electrons in Ga do not screen the nuclear charge effectively and the outer electrons experience more force of attraction and thereby causing decrease in its radius.
- 5. Density increases from boron to thallium. However, boron and aluminium have comparatively low values.
- 6. The melting points decrease from B to Ga and then increase from Ga to Tl. The high melting point of boron is due to the fact that it exists as a giant covalent polymer in both solid and liquid state. Gallium has an unusual structure. It consists of only Ga<sub>2</sub> molecules. Gallium melting point is 30°C and it exists as a liquid up to 2000°C and hence used in high temperature thermometry.
  - Al, In and Tl all have closed packed metal structures. However, boiling points follow a regular decrease from B to Tl.
- 7. Since p electrons are held less tightly than s electrons, the first ionisation energy of each element is rather low as compared to first ionisation energy of alkaline earth metal of

the same period. The second and third ionisation energies are considerably higher. The sum of three ionisation energies of these elements change in oscillating manner. B has maximum value. It decreases from B to Al, increases from Al to Ga, again decreases from Ga to In and then increases from In to Tl.

- Boron having very high ionisation energy is least electropositive, i.e., regarded as more non-metallic. Aluminium is most metallic or electropositive. The remaining three are weakly metallic in nature.
- B and Al exhibit an oxidation state of +3. Ga, In and Tl show +1 and +3 oxidation state due to inert pair effect.

Relative stability of +3 and +1 oxidation states can be given

B > Al > Ga > In > Tl + 3 stability decreases from B to Tl B < Al < Ga < In < Tl + 1 stability increases from B to Tl Tl<sup>3+</sup> ions show oxidising properties as these are converted into Tl<sup>+</sup> ions. Gallium appears to show +2 oxidation state in GaCl<sub>2</sub>. However, it is believed that this compound has structure Ga [GaCl<sub>4</sub>] which contains univalent and trivalent gallium ions.

- The bonding in the compounds of IIIA elements is mainly covalent due to following reasons:
  - (a) small size of ions and their high charge are responsible for high polarisation,
  - (b) the sum of three ionisation energies is very high,
  - (c) the electronegativity values are high,

Boron always shows covalency. Many simple compounds of other elements such as AlCl3 and GaCl3 are covalent when anhydrous. However, Al, Ga, In and Tl form metal ions in solutions as the hydration energies are very high.

Thallium compounds are ionic in nature.

- 11. Group IIIA elements form complexes much more readily than s-block elements because of their small size, increased charge and availability of vacant orbitals.
- Finely divided impure boron burns in air forming oxide while pure boron is less reactive.

Aluminium reacts with air forming its oxide which protects it from further action. The oxide film on Al is so useful that in industry it is purposely increased by an electrolytic process called anodising. Anodised cooking vessels are used as nonstick cookware. Ga and In are not affected in air. Tl forms an oxide on its surface.

- Boron is not affected by water or steam. Al decomposes cold water if the oxide layer is not present on its surface. Ga and In are attacked by water only in presence of oxygen. Tl is attacked by moist air.
- Boron is not affected by non-oxidising acids while other eléments dissolving forming trivalent salts. The oxidising acids attack all the elements. However, Al and

Ga become passive with conc. HNO<sub>3</sub>.

- 15. B, Al and Ga react with alkali solutions evolving H<sub>2</sub>. In and Tl are not affected.
- 16. All these elements combine with halogens forming corresponding halides.

Boron and aluminium combine with nitrogen and carbon on heating to form nitrides and carbides respectively.

The structure of boron nitride (BN) is similar to the structure of graphite. Recently, a crystalline form of boron nitride called borazon has been synthesised by application of high temperature and pressure. This form is even harder than diamond. It is used as abrasive. Boron carbide (B<sub>4</sub>C) is the hardest known artificial substance and is called norbide.

- 17. Boron combines with metals on heating to form borides. The rest of the elements do not combine with metals.
- All the members of group IIIA form oxides of the type  $M_2O_3$ . On moving down the group, there is gradual change from acidic to amphoteric and then to basic character.

Thallium also forms Tl<sub>2</sub>O which is more stable and behaves as alkali metal oxide.

**19.** All these elements form hydroxides of the type  $M(OH)_3$ . The basic nature of the hydroxides increases down the group. B(OH)<sub>3</sub>·(H<sub>3</sub>BO<sub>3</sub>) is acidic. B(OH)<sub>3</sub> coordinates with OH<sup>-</sup> group of water releasing proton.

$$B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$$

It reacts with NaOH to produce the sodium salt.

B(OH)<sub>3</sub> + NaOH 
$$\rightleftharpoons$$
 Na[B(OH)<sub>4</sub>]  $\frac{-2H_2O}{\sqrt{}}$  NaBO<sub>2</sub> (Sodium metaborate)

Boric acid contains triangular BO<sub>3</sub><sup>3-</sup> ion in which boron lies in sp<sup>2</sup> hybrid state. In solid state, B(OH)<sub>3</sub> units are hydrogen bonded to form two dimensional sheet.

Al(OH)<sub>3</sub> and Ga(OH)<sub>3</sub> are amphoteric as the tendency to rupture O-H bond decreases as the size of the ion increases. In(OH)<sub>3</sub> and Tl(OH)<sub>3</sub> are basic in nature.

- 20. The elements of group IIIA do not directly combine with hydrogen. However, a number of hydrides are known. Boron forms a number of stable covalent hydrides with a general formulae  $B_nH_{n+4}$  and  $B_nH_{n+6}$ . These are called boranes. Boranes are electron deficient compounds. The expected BH<sub>3</sub> is unknown. Aluminium forms a polymeric hydride,  $(AlH_3)_n$  known as alane. Gallium forms dimeric hydride, Ga<sub>2</sub>H<sub>6</sub> (digallane) and indium form a polymeric hydride. Thallium does not form any hydride.
  - B, Al and Ga form complex anionic hydrides such as NaBH<sub>4</sub>, LiAlH<sub>4</sub> and LiGaH<sub>4</sub>.
- 21. All the elements of group IIIA form trihalides. The boron halides are covalent. The boron halides act as Lewis acids. All boron halides except BF3 are hydrolysed to boric acid. BF3 forms an addition product with water as B-F bond is very strong.

$$BF_3 + H_2O \Longrightarrow H^+[BF_3OH]^- \xrightarrow{H_2O} H_3O^+[BF_3OH]^-$$

Boron halides for complex halides of the type  $H[BF_4]$ . The trifluorides of Al, Ga, In and Tl are ionic while the chlorides, bromides and iodides are largely covalent when anhydrous. However, their covalent nature decreases on moving from Ga to Tl. Trihalides fume in air and undergo hydrolysis. They also act as Lewis acids. However, this tendency decreases with increase in size of the cation. The form complex halides of the type  $[MX_6]^{3-}$ . They have the tendency to complete their octet by forming **dimers**. Dimer forms exist in vapour state and in non-polar solvents. Dimer structures disappear when dissolved in water. This is due to high hydration energy, when  $[M(H_2O)_6]^{3+}$  and  $3X^-$  ions are formed.

$$AlCl_3 + 9H_2O \longrightarrow [Al(H_2O)_6] (OH)_3 + 3H^+ + 3Cl^-$$

- 22. The important minerals of boron are:
  - (a) Borax, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O,
  - (b) Colemanite, Ca<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·5H<sub>2</sub>O,
  - (c) Boric acid, H<sub>3</sub>BO<sub>3</sub>.

Borax is also called **Tincal** or **Suhaga**. Tincal contains about 45% borax. Natural tincal is dissolved in hot water and insoluble impurities are filtered off. The solution is concentrated and cooled when crystals of borax are obtained. It exists in three forms (a) Prismatic borax—Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O (b) Octahedral—Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·5H<sub>2</sub>O. This is **Jeweller's borax**. It is obtained by crystallising solution at 60°C (c) Anhydrous—Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. It is also called borax glass. It is not stable form as it absorbs moisture and gradually converted into decahydrate form. The solution of borax is alkaline in nature as it is a salt of a weak acid and strong alkali.

On heating if first swells up due to elimination of water and then melts which solidifies to transparent glassy bead.

$$\begin{array}{c} Na_{2}B_{4}O_{7}\cdot 10H_{2}O \xrightarrow{Heat} & Na_{2}B_{4}O_{7} \\ \hline & -10H_{2}O & Anhydrous \\ \hline & \hline & 2NaBO_{2} + B_{2}O_{3} \\ \hline & Glassy bead \end{array}$$

When the hot glassy bead is brought in contact with a coloured salt and heated again inflame, B<sub>2</sub>O<sub>3</sub> displaces volatile oxides to form metaborates. Metaborates exhibit characteristic colours. This is known as **borax bead test.** 

Colour of metaborates Blue Green Blue Green Brown

**23.** Boron is known to exist in two forms (a) amorphous and (b) crystalline.

Amorphous boron is obtained by reduction of B<sub>2</sub>O<sub>3</sub> with Na or K or Mg at high temperature in a covered crucible.

Crystalline form is obtained by the reduction of  $B_2O_3$  with Al—powder. Crystalline boron is black and chemically inert in nature. It is very hard. Amorphous boron is brown and chemically active. Boron is used as a deoxidiser in the casting of copper and for making boron steel which are used as control rods in nuclear reactors.

**24.** Diborane is the simplest hydride of boron. It is prepared by action of LiAlH<sub>4</sub> on boron trichloride in ether or by reacting lithium hydride with boron trifluoride. It is a colourless gas which is stable at room temperature. It has disagreeable odour and causes headache. It burns in air and reaction is highly exothermic. It is decomposed by water and alkalies liberating hydrogen. At low temperature, it forms an addition product with ammonia (B<sub>2</sub>H<sub>6</sub>·2NH<sub>3</sub>). When this product is heated at 200°C, a volatile compound, **borazole or inorganic** 

**benzene**  $(B_3N_3H_6)$  is formed which has structure similar to benzene.

In diborane molecule, four hydrogen atoms and two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. Each boron atom forms four bonds though it has three electrons. Each bridge hydrogen atom is bonded to two boron atoms by sharing of two electrons. Such a covalent bond is called three centre electron pair bond or banana bond. Every boron atom is  $sp^3$ -hybridized. Diborane is used for making high energy fuels and propellants.

- **25.** On heating borazine, a product similar to naphthalene known as inorganic naphthalene is formed.
- **26.** The relative Lewis acid character of boron trihalides is found to follow the order:

$$BI_3 > BBr_3 > BCl_3 > BF_3$$

This is due to back donation by smaller halogen atoms to boron atom, *i.e.*, forming  $p\pi - p\pi$  bond. This tendency is maximum in fluorine and decreases from F to I as the size increases.

- 27. Aluminium is extracted from bauxite ore (Al<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O). It is usually contaminated with ferric oxide and silica. The removal of these impurities is very essential before the pure alumina is put to electrolytic reduction. The removal is done by the application of the following processes.
  - (a) **Baeyer's process**—Applied when Fe<sub>2</sub>O<sub>3</sub> is the chief impurity. Conc. solution of NaOH used.
  - (b) Hall's process—Sodium carbonate is used.
  - (c) Serpeck's process—The ore is mixed with coke and nitrogen is passed at 1800°C.

AlN is formed which is hydrolysed into Al(OH)<sub>3</sub>. This method is applied when silica is present in abundance. Ammonia is obtained as a by-product.

The electrolysis of pure alumina presents two difficulties.

- (i) It is bad conductor of electricity.
- (ii) The melting point is about 2000°C.

These difficulties are overcome by using a mixture containing alumina, cryolite (Na<sub>3</sub>AlF<sub>6</sub>) and fluorspar (CaF<sub>2</sub>) in the ratio of 20: 40: 20. The fusion temperature of this mixture is 900°C and the mixture is good conductor of electricity. The electrolysis is carried out in an iron box lined by gas carbon which acts as cathode. The anode consists carbon rods. The overall chemical reaction is :  $2Al_2O_3 \longrightarrow 4Al + 3O_2$ 

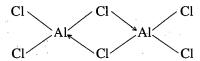
Al of 99.8% purity is obtained. It is further purified by Hoope's electrolytic process.

- **28.** Because of its lightness, good conductivity and resistance to corrosion, it is used for making alloys. The important alloys are:
  - (a) Magnalium (95% Al + 5% Mg)
  - (b) Duralumin (95% Al + 4% Cu + 0.5% Mg + 0.5% Mn)
  - (c) Aluminium bronze (90% Cu + 9.5% Al + 0.5% Sn)
  - (d) Nickeloy (95%Al + 4% Cu + 1% Ni)
  - (e) γ-alloy (93% Al + 4% Cu + 2% Ni + 1% Mg)
  - (f) Alnico (77% Steel + 2% Ni + 20% Al + 1% Co)

Thin foils of Al are used for wrapping soaps, cigarettes and confectionery. Al wire is used in transmission lines and coils

for dynamos and motors. It is also used for making silvery paints and in thermite process.

29. Anhydrous AlCl<sub>3</sub> is prepared by passing dry HCl or Cl<sub>2</sub> gas over heated aluminium turnings in absence of air. It is also obtained by passing Cl<sub>2</sub> gas over heated mixture of Al<sub>2</sub>O<sub>3</sub> and coke. It is used as a catalyst in Friedel-Craft's reaction. The molecule is an autocomplex and is represented as:



Anhydrous AlCl<sub>3</sub> is a Lewis acid. Anhydrous form is covalent while hydrated form AlCl<sub>3</sub> 6H<sub>2</sub>O is ionic.

**30.** The term alum is used to describe any double sulphate having the composition  $M_2SO_4 \cdot M_2'(SO_4)_3 \cdot 24H_2O$ , where M stands for monovalent basic radical and M' for a trivalent basic radical.

The most commonly known alum is potash alum,  $K_2SO_4$ ·Al<sub>2</sub>( $SO_4$ )<sub>3</sub>·24H<sub>2</sub>O. It is used in purification of water, as an antiseptic and in stopping bleeding, as a mordant in dyeing and in leather tanning.

- Ultramarine is an artificial Lapis-Lazuli, a rare mineral (Na<sub>3</sub>Al<sub>3</sub>Sr<sub>3</sub>S<sub>3</sub>O<sub>12</sub>) which has fine blue colour. It is used in making blue paint.
- 32. Highly toxic element of group IIIA or 13 is thallium.
- 33. Precious stones such as sapphire, ruby, topaz, etc., are Al<sub>2</sub>O<sub>3</sub> containing oxides of other metals.
- 34. Double sulphates of divalent ions and trivalent ions with 24 water molecules of crystallisation are called **pseudoalums**, e.g., MSO<sub>4</sub>·M<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O. These are not isomorphous with alums.
- **35.** Aluminium acetate is commonly known as **red liquor** which is used as a mordant in dyeing and calico printing.

# - • • • - PRACTICE PROBLEMS - • • • -

### ■ Subjective Type Questions

#### 1. Answer the following:

- (a) Which element among group 13 elements has the highest ionisation enthalpy?
- (b) Which has higher ionisation enthalpy?

#### Al or Ga

- (c) Name the element of group 13 which forms the most stable compounds in +1 oxidation state.
- (d) Name the metal which is commonly used as a reducing agent in metallurgical operations.
- (e) Name the most abundant metal in the earth's crust. To which group does it belong?
- (i) By means of a balanced equation show how H<sub>3</sub>BO<sub>3</sub> behaves as an acid in water.
  - (ii) Anhydrous aluminium chloride is used as a catalyst. Explain.
  - (iii) Which elements of group 13 form amphoteric hydroxides.?
  - (iv) Why boron is unable to form  $[BF_6]^{3-}$  ion?
  - (v) Does Ga has +2 oxidation state in GaCl<sub>2</sub>?
- 3. (i) What are basic units in the structure of orthoboric acid? How are they linked?
  - (ii) What types of bonds are present in diborane?
  - (iii) What is the nature of boron halides?
  - (iv) Why boron halides do not exist as dimers? Why AlCl<sub>3</sub> exists as Al<sub>2</sub>Cl<sub>6</sub>?
  - (v) Explain briefly why boron trichloride is a gas and aluminium trichloride is a dimer solid.

#### 4. Give formula of the following:

- (a) (i) Panderinite
- (ii) Rasorite [M.L.N.R. 1996]
- (iii) Jeweller's borax
- (iv) Feldspar
- (v) Cryolite
- (vi) Corundum
- (vii) Alunite
- (viii) Turquoise
- (ix) Colemanite
- (x) Mica

(b) Write the formulae of the compounds, you would expect B and Al to form with halogens, oxygen, sulphur, nitrogen and carbon.

#### 5. Answer the following:

- (i) What is the outer electronic configuration of group IIIA elements?
- (ii) Name the first two elements of group IIIA.
- (iii) What is Tincal?
- (iv) What is thermite mixture?
- (v) What is inorganic benzene?
- (vi) Name the two metals present in common alum.
- (vii) Name the aluminium compound used in Friedel-Craft's reaction.
- (viii) What is silver paint?
- (ix) Name the metal which is commonly used as a reducing agent in metallurgical operations.
- (x) Name the compound of aluminium which is used as germicide and coagulant in the purification of water.

#### 6. What happens when?

- Dry chlorine gas is passed over hot mixture of alumina and coke.
- (ii) Borax is heated strongly.
- (iii) Excess of caustic soda is added to a solution of aluminium chloride.
- (iv) Water is added to aluminium nitride.
- (v) Water is added to aluminium carbide.
- (vi) Aluminium is heated with caustic soda solution.

[L.I.T. 1997]

- (vii) A mixture of borax and cobalt oxide is heated in flame.
- (viii) Alum is heated.
- (ix) Alum is added to copper sulphate solution.
- (x) Aluminium reacts with HNO<sub>3</sub>.
- 7. Starting from borax, how would you obtain?
  - (i) Boric acid, (ii) Boron trioxide, (iii) Boron,
  - (iv) Boron nitride, (v) Boron trichloride.

- 8. Starting from alumina, how would you obtain?
  - (i) Potash alum,
  - (ii) Anhydrous aluminium chloride,
  - (iii) Aluminium nitride, (iv) Sodium aluminate.
- 9. How you will obtain?
  - (i) Anhydrous aluminium chloride from potash alum.
  - (ii) Aluminium bromide from aluminium chloride.
  - (iii) Aluminium sulphate from potash alum.
  - (iv) Alum from aluminium.
- 10. Give an account for the following:
  - (a) No visible reaction occurs when aluminium is left in contact with concentrated nitric acid. [M.L.N.R. 1991]
  - (b) The hydroxides of aluminium and iron are insoluble in water. However, NaOH is used to separate one from the other. [I.I.T. 1991]
  - (c) Anhydrous aluminium chloride cannot be prepared by heating hydrated AlCl<sub>3</sub>·6H<sub>2</sub>O.
  - (d) Aluminium vessels should not be cleaned with cleansing agent containing washing soda.
  - (e) Duralumin is used in aircraft industry.
- 11. Explain the following with relevant reason.
  - (i) Aluminium vessels can be used to store concentrated nitric acid.

[**Hint**: HNO<sub>3</sub> forms a protective film, Al<sub>2</sub>O<sub>3</sub>, on the walls of the containers which is not acted upon by conc. HNO<sub>3</sub>.]

(ii) AlCl<sub>3</sub> forms a dimer but BCl<sub>3</sub> does not form dimer.

[Hint: AlCl<sub>3</sub> lacks back bonding as in BCl<sub>3</sub> because of increase in size of aluminium. Aluminium metal

atoms complete their octet by coordinate bond forming bridges by chlorine atoms between two Al atoms.]

(iii) Aluminium metal is frequently used as reducing agent for the extraction of metals such as Cr, Mn, Fe, etc.

[Hint: Al has great affinity for oxygen. Al, thus, removes oxygen from the oxides of less electropositive metals and acts as reducing agent.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$
;  $\Delta H = -ve$ 

(iv) Aluminium cannot be prepared by the electrolysis of aqueous solution of its salt.

[Hint: Discharge potential of aluminium is higher than the discharge potential of hydrogen. Thus, the aqueous solution containing Al<sup>3+</sup> and H<sup>+</sup> ions, when electrolysed, the H<sup>+</sup> ions rather than Al<sup>3+</sup> ions are discharged at cathode and hydrogen is evolved.]

(v) The B—X distance is shorter than what is expected theoretically in B $X_3$  molecule (X = Cl, F, Br, I)?

[Hint: The bond B—X in BX<sub>3</sub> has double bond character due to back bonding. This brings resonance in the molecule which is responsible for shorter B—X distance than expected.

$$\dot{\bar{X}} = -\bar{\bar{B}} \stackrel{X}{\swarrow} \longleftrightarrow X - \bar{\bar{B}} \stackrel{\bar{\bar{X}}}{\swarrow} \longleftrightarrow X - \bar{\bar{B}} \stackrel{X}{\swarrow} ]$$

(vi) Although the ionisation potential of boron (8.30 eV) is less than gold (9.22 eV), yet former is a non-metal while the latter is a metal.

[Hint: This is due to structural difference in the solid states. In general, metals have large number of atoms as neighbours while non-metals have relatively less number of atoms as neighbours. Gold has 12 atoms as neighbours while boron has 6 or less atoms as neighbours in solid states.]

(vii) Why boron does not form B<sup>3+</sup> ion?

[Hint: The total sum of all the three ionisation energies of boron is so high that lattice energy liberated by interaction of B<sup>3+</sup> and anions is not enough for formation of this ion.]

(viii) Aluminium fluoride is ionic while AlCl<sub>3</sub> is covalent.

[Hint: The size of chloride ion is larger than fluoride ion. Due to higher polarisation in AlCl<sub>3</sub>, it behaves as a covalent compound. The electronegativity difference between Al and Cl is 1.5 while between Al and F it is 2.5. Thus, the bond between Al and F is ionic and between Al and Cl covalent in nature.]

(ix) First ionisation potential of Al is lower than that of Mg. [Hint: The electronic configuration of Al and Mg are 1s<sup>2</sup>, 2s<sup>2</sup> 2p<sup>6</sup>, 3s<sup>2</sup> 3p<sup>1</sup> and 1s<sup>2</sup>, 2s<sup>2</sup> 2p<sup>6</sup>, 3s<sup>2</sup> respectively. It is easier to remove electron from unpaired p-orbital than the paired s-orbital.]

(x) Borazine is more reactive than benzene.

[Hint: In benzene, C=C bonds are non-polar while in borazine, the bonds between boron and nitrogen are polar. Addition is frequent in borazine, the more negative group generally attaches to boron atoms.]

(xi) Certain metallic oxides are reduced with aluminium rather than with carbon during extraction.

[Hint: The metals which react with carbon to form carbides are extracted from their oxides by using aluminium as a reducing agent as it has high affinity for oxygen.]

[Hint: It dissolves in acid as well as in alkali.]

12. Write short notes on the following:

(xii) Al(OH)<sub>3</sub> is amphoteric.

- (i) Goldschmidt alumino-thermic process.
- (ii) Ultramarines.
- (iii) Alums.
- (iv) Electrolytic refining of aluminium metal.
- (v) Relative strength of boron halides as Lewis acids.
- (vi) Borax bead test.
- **13.** Describe the preparation, properties and uses of following compounds:
  - (i) Borax. (ii) Potash alum.
  - (iii) Anhydrous aluminium chloride.
  - (iv) Boric acid. (v) Borazine.
- **14.** Compare the properties of boron and aluminium under the following heads:
  - (i) Electronic configuration.
- (ii) Nature of oxides.

[M.L.N.R. 1994]

- (iii) Nature of chlorides.(v) Nature of hydrides.
- (iv) Action of acids.(vi) Nature of nitrides.
- 15. A certain salt (X) gives the following tests:
  - (i) Its aqueous solution is alkaline to litmus.

- (ii) On strongly heating it swells to give a glassy bead.
- (iii). When concentrated sulphuric acid is added to a hot concentrated solution of (X), white crystals of a weak acid separate out. Identify (X) and write down, the chemical equations for reactions at steps (i), (ii) and (iii).

[Roorkee 1992]

**[Hint:** (X) is borax, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O

(i) 
$$Na_2B_4O_7 + 7H_2O \Longrightarrow 2NaOH + 4H_3BO_3$$
  
(Strong) (Weak)

Due to presence of NaOH, the aqueous solution is alkaline to litmus.

(ii) 
$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\text{Heat} \text{ swells}} Na_2B_4O_7 + 10H_2O \xrightarrow{\text{Swells}} 2NaBO_2 + B_2O_3$$
Glassy bead

(iii) 
$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

- **16.** A white crystalline compound (A) swells upon heating and gives violet coloured flame on bunsen flame. Its aqueous solution gives the following reactions.
  - (a) A white precipitate with BaCl<sub>2</sub> in presence of HCl.
  - (b) When treated with excess of NH<sub>4</sub>OH, it gives white gelatinous precipitate. The white precipitate dissolves in NaOH and reappears on boiling with concentrated solution of NH<sub>4</sub>Cl.
  - (c) It gives yellow precipitate with cobaltinitrite solution. Identify the compound (A) and explain the reactions.

**Hint:** The compound (A) is potash alum, K<sub>2</sub>SO<sub>4</sub>·Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O. It swells upon heating due to evolution of water molecules.

$$K_2 SO_4 \cdot Al_2 (SO_4)_3 \cdot 24 H_2 O \xrightarrow{\text{Heating swells up}} K_2 SO_4 \cdot Al_2 (SO_4)_3 + 24 H_2 O$$

It gives violet colour to flame due to presence of potassium salt.

(a) The solution consists sulphate ions which combine with Ba<sup>2+</sup> ions to form white insoluble precipitate.

$$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4$$

(b) With NH<sub>4</sub>OH, aluminium hydroxide is precipitated which dissolves in NaOH forming sodium meta-aluminate.

$$Al_2(SO_4)_3 + 6NH_4OH \longrightarrow 2Al(OH)_3 + 3(NH_4)_2SO_4$$

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$
Soluble

The solution on heating with ammonium chloride gives a precipitate of Al(OH)<sub>3</sub>.

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow Al(OH)_3 + NaCl + NH_3$$

(c) Potassium salt gives yellow precipitate with cobaltinitrite

$$2K_2SO_4 + Na_4[Co(NO_2)_6] \longrightarrow K_4[Co(NO_2)_6] + 2Na_2SO_4]$$
Yellow ppt.

- 17. An inorganic compound (A) shows the following reactions:
  - (i) It is white solid, exists as dimer and fumes in wet air.
  - (ii) It sublimes at 180°C and forms monomer if heated to 400°C.
  - (iii) Its aqueous solution turns blue litmus to red and gives a white precipitate with AgNO<sub>3</sub> solution which is soluble in NH<sub>4</sub>OH.

(iv) Addition of NH<sub>4</sub>OH and NaOH separately to the solution of (A) gives a gelatinous precipitate which is, however, soluble in excess of NaOH. Identify the compound (A).

[Ans. (A) is  $Al_2Cl_6$ ]

18. The metallic salt XY is soluble in water.

When the solution is treated with NaOH solution, a white precipitate (A) is formed. This precipitate is soluble in excess of NaOH solution to form a compound (B). When this solution is boiled with solid NH<sub>4</sub>Cl, a precipitate of a compound (C) is formed. An aqueous solution of XY upon treatment with BaCl<sub>2</sub> solution gave a white precipitate (D) which was insoluble in dilute HCl. The salt XY forms a double salt with potassium sulphate.

[Ans. 
$$XY = Al_2(SO_4)_3$$
; [A] = Al(OH)<sub>3</sub>; [B] = NaAlO<sub>2</sub>; [C] = Al(OH)<sub>3</sub>; [D] = BaSO<sub>4</sub>]

- **19.** Furnish the following information in connection with the extraction of aluminium by the electrolytic process:
  - (i) the composition of the electrolyte;
  - (ii) the reactions that take place at the electrodes;
  - (iii) the component of the electrolyte consumed;
  - (iv) collection of the extracted metal;
  - (v) the nature of the electrodes;
  - (vi) the temperature of electrolysis;
  - (vii) the role of different components of the electrolyte in the process of extraction.
- 20. Compound (X) on reduction with LiAlH<sub>4</sub> gives a hydride (Y) containing 21.72% hydrogen along with other products. The compound (Y) reacts with air explosively resulting in boron trioxide. Identify (X) and (Y). Give balanced reactions involved in the formation of (Y) and its reaction with air. Draw the structure of (Y). [I.I.T. 2001]

[Hint: 
$${}^{4}BCl_{3} + 3LiAlH_{4} \longrightarrow {}^{2}B_{2}H_{6} + 3AlCl_{3} + 3LiCl_{3}$$
  
% of hydrogen in  ${}^{6}B_{2}H_{6} = \frac{6}{27.62} \times 100 = 21.72$   
 ${}^{6}B_{2}H_{6} + 3O_{2} \xrightarrow{Explosion} {}^{2}B_{2}O_{3} + 3H_{2}O$ 

Structure of 
$$B_2H_6$$
  $H$   $H$   $H$   $H$   $H$   $H$ 

**21.** (a) How is boron obtained from borax? Give chemical equations with reaction conditions. Write the structure of B<sub>2</sub>H<sub>6</sub> and its reaction with HCl. [I.I.T. 2002]

[Hint: See the text.]

(b) Write balanced equations for reactions of  $BF_3$  and  $Al_4C_3$  with water. [I.I.T. 2002]

[Hint: 
$$4BF_3 + 6H_2O \longrightarrow H_3BO_3 + 3H_3^{\dagger}O + 3BF_4^{\dagger}$$
  
 $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$ ]

### ■ Matching Type Questions

#### Match the following:

- [A] (a) Anhydrous AlCl<sub>3</sub>
  - (b) Alum
  - (c) Ultramarine

(b) Cryolite -

(c) Bauxite

(d) Borax

- (d) Borax
- (i) Antiseptic
- (ii) Alloy
- (iii) Friedel-Crafts reaction
- (iv) Complex blue coloured silicate
- (e) Magnelium (v) Tincal
- **B** (a) Colemanite (i) Na<sub>3</sub>AlF<sub>6</sub>
  - (ii) KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O
    - (iii) Ca<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·5H<sub>2</sub>O
    - (iv) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O
  - (e) Potash alum (v) A1<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O

- [C] (a) Inorganic benzene
- (i) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O
- (b) Jeweller's borax (ii)  $B_2H_6$
- (c) Borax
- (iii) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·5H<sub>2</sub>O
- (d) Diborane
- (iv) Mordant (v)  $B_3N_3H_6$
- (e) Alum
- (i) Building ships and
- (a) Good thermal conductivity
- aircrafts
- (b) Good electrical conductivity
- (ii) Utensils
- (c) Low density and resistance to corrosion
- (iii) Electric wires
- (d) Non-toxicity
- (iv) Adsorbent
- (e) Gel nature of Al(OH)<sub>3</sub> (v) Food packing

## tuswers

### Answers: Subjective Type Questions

1. (a) Boron

2.

- (b) Gallium
  - (c) Thallium
- (d) Aluminium (e) Aluminium, Group 13
- (i)  $B(OH)_3 + H \longrightarrow [B(OH)_4]^- + H^+$
- (ii) At atom in AlCl<sub>3</sub> has only 6 electrons in its valence shell. It needs two more electrons to complete its octet. It acts as a Lewis acid in reaction. It helps to generate electrophile  $R^+$  or RCO+, etc., which attacks benzene, i.e., the aromatic ring.
- (iii) Aluminium and gallium

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

$$2Al(OH)_3 + 2NaOH + 6H_2O \longrightarrow 2NaAl(OH)_4 + 3H_2$$

$$Ga(OH)_3 + 3HCl \longrightarrow GaCl_3 + 3H_2O$$

$$2Ga(OH)_3 + 2NaOH + 6H_2O \longrightarrow 2NaGa(OH)_4 + 3H_2$$

- (iv) Boron cannot expand octet due to absence of d-orbitals in the valence shell.
- (v) GaCl<sub>2</sub> is actually Ga<sub>2</sub>Cl<sub>4</sub>, i.e., Ga<sup>+</sup>[Ga<sup>3+</sup>Cl<sub>4</sub>]. Ga has thus +1 and +3 oxidation states and not +2.
- (i) The basic units are BO<sub>3</sub><sup>3</sup> ions which are linked through hydrogen bonds. (ii) There are two types of bonds in diborane two electron normal
  - bonds and three centred two electron bonds.
  - (iii) Boron halides are electron deficient compounds. They act as Lewis acids.
  - (iv) Boron atom being small in size is unable to accommodate four large sized halogen atoms around it.
  - (v) In BCl<sub>3</sub>, boron attains an octet of electrons by means of  $p\pi$ - $p\pi$  bonding between B and Cl atoms. Thus, it exists as a monomeric gas. Due to large size of Al, efficient  $p\pi$ - $p\pi$  bonding cannot occur. Thus, AlCl<sub>3</sub> dimerises to attain an, octet by forming adative bond between Cl and Al atoms. Thus, it exists as a solid.
- (a)
  - (i)  $Ca_2B_6O_{11} \cdot 3H_2O_{11}$
- (ii) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·4H<sub>2</sub>O,
- (iii) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·5H<sub>2</sub>O<sub>7</sub>
- (iv) KAlSi<sub>3</sub>O<sub>8</sub>,
- (v) Na<sub>3</sub>AlF<sub>6</sub>,
- (vi) Al<sub>2</sub>O<sub>3</sub>,
- (vii)  $K_2SO_4$ · $Al_2(SO_4)_3$ · $4Al(OH)_3$ ,(viii)  $AlPO_4$ · $Al(OH)_3$ · $H_2O$ ,
- (ix)  $Ca_2B_6O_{11} \cdot 5H_2O$ ,
- (x)  $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$ .
- (b) Formulae of the compounds of boron and aluminium: BX3 and AlX<sub>3</sub>, B<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>S<sub>3</sub> and Al<sub>2</sub>S<sub>3</sub>, BN and AlN,  $B_{12}C_3$  and  $Al_4C_3$ .

- 5. (i)  $ns^2 np^1$ , (ii) Boron and aluminium, (iii) It is a mineral of boron. Its composition is Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 10H<sub>2</sub>O, (iv) Mixture containing 1 part Al powder and 3 parts Fe<sub>2</sub>O<sub>3</sub>, (v) Borazole or borazine, B<sub>3</sub>N<sub>3</sub>H<sub>6</sub> is known as inorganic benzene, (vi) Common alum is the double sulphate of potassium and aluminium. Its composition is, K<sub>2</sub>SO<sub>4</sub>·Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O, (vii) Anhydrous aluminium chloride, AlCl<sub>3</sub>, (viii) Finely divided aluminium powder suspension in linseed oil, (ix) Aluminium, (x) Common alum, K<sub>2</sub>SO<sub>4</sub>·Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O.
- $Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$ 
  - (ii)  $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{-10H_2O} Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$
  - $AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$ (iii)

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

- $AIN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$ (iv)
- $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$ (v)
- (vi)  $2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$
- (vii)  $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{-10H_2O} Na_2B_4O_7 \rightarrow 2NaBO_2 + B_2O_3$  $B_2O_3 + CoO \longrightarrow Co(BO_2)_2$ Cobalt metaborate
- (viii) It melts and loses water of crystallisation up to 200°C and white porous mass is obtained on red heat. This white mass is known as burnt alum.

$$\begin{array}{c} K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \xrightarrow{200^{\circ}C} K_2SO_4 \cdot Al_2(SO_4)_3 + 24H_2O \\ K_2SO_4 \cdot Al_2(SO_4)_3 \xrightarrow{\text{Red heat}} K_2SO_4 + Al_2O_3 + 3SO_3 \end{array}$$

(ix) Being more electropositive, it displaces copper from copper sulphate.

$$3\text{CuSO}_4 + 2\text{Al} \longrightarrow \text{Al}_2 (\text{SO}_4)_3 + 3\text{Cu}$$

- (x) Nitric acid whether dilute or concentrated hardly affects aluminium at all. Aluminium is rendered passive. A thin film of Al<sub>2</sub>O<sub>3</sub> is formed on the surface of the metal.
- (i)  $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4$ 
  - (ii)  $2H_3BO_3 \xrightarrow{Strongly} B_2O_3 + 3H_2O$
  - $B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$
  - (iv)  $Na_2B_4O_7 + 2NH_4C1 \longrightarrow 2BN + B_2O_3 + 2NaCl + 4H_2O$
  - $B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$

8. (i)  $Al_2O_3 + 3H_2SO_4 \xrightarrow{Boiled} Al_2(SO_4)_3 + 3H_2O_4$ 

Calculated quantity of K2SO4 is added to above solution. The solution is cooled when crystals of alum are obtained.

 $Al_2(SO_4)_3 + K_2SO_4 + 24H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ 

- $Al_2O_3 + 3C + 3Cl_2 \xrightarrow{1000^{\circ}C} 2AlCl_3 + 3CO$
- $Al_2O_3 + 3C + N_2 \xrightarrow{1800^{\circ}C} 2AlN + 3CO$ (iii)
- $Al_2O_3 + 6NaOH \xrightarrow{Fused} 2Na_3AlO_3 + 3H_2O$ (iv)
- (i)  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O + 6NH_4OH \longrightarrow$

$$K_2SO_4 + 3(NH_4)_2SO_4 + 2AI(OH)_3 + 24H_2O_{ppt}$$

$$2Al(OH)_3 \xrightarrow{\text{Heat}} Al_2O_3 + 3H_2O$$

$$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{1000^{\circ}C} 2AlCl_3 + 3CO$$

 $AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3 + 3NH_4Cl$ 

$$Al(OH)_3 + 3HBr \longrightarrow AlBr_3 + 3H_2O$$
  
 $Al(OH)_3 \xrightarrow{Heat} Al_2O_3 + 3H_2O$ 

$$Al_2O_3 + 3C + 3Br_2 \longrightarrow 2AlBr_3 + 3CO$$

(iii) Potash alum + NH<sub>4</sub>OH → Al(OH)<sub>3</sub>

$$2Al(OH)_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 6H_2O$$

(iv) Al 
$$\xrightarrow{\text{H}_2\text{SO}_4}$$
 Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  $\xrightarrow{\text{K}_2\text{SO}_4 \text{ soln.}}$   $\xrightarrow{\text{Solution is}}$  K<sub>2</sub>SO<sub>4</sub>·Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O  $\xrightarrow{\text{Solution is}}$ 

- 10. (a) Aluminium is rendered passive.
  - (b) Al(OH)<sub>3</sub> dissolves in NaOH while Fe(OH)<sub>3</sub> remains insoluble.

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

(c) Hydrolysis of AlCl<sub>3</sub> occurs into Al<sub>2</sub>O<sub>3</sub>.

$$2AICl_3 + 3H_2O \longrightarrow Al_2O_3 + 6HCl_3$$

- (d) Aluminium dissolves in caustic alkalies.
- (e) Duralumin is an alloy of aluminium (95%), Cu (4%), Mg (0.5%) and Mn (0.5%). It is light and tough. It is resistant to corrosion.
- 19. (i) Pure Al<sub>2</sub>O<sub>3</sub> 20%; Cryolite Na<sub>3</sub>AlF<sub>6</sub> 60%; Fluorspar CaF<sub>2</sub>
  - (ii) Reactions at electrodes,

At cathode: 
$$Al^{3+} + 3e \longrightarrow Al$$

At anode:

$$2F^- \longrightarrow F_2 + 2e$$

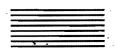
$$2Al_2O_3 + 6F_2 \longrightarrow 4AlF_3 + 3O_2$$

- (iii) The component consumed during electrolysis, Al<sub>2</sub>O<sub>3</sub>.
- (iv) The liberated metal in the molten state is taken out through an outlet near the bottom of the electrolytic cell.
- (v) Carbon lining of the electrolytic cell acts as cathode and carbon rods act as anode.
- (vi) 950°C.
- (vii) Molten cryolite acts as the solvent for Al<sub>2</sub>O<sub>3</sub>. Fluorspar decreases the viscosity of the mixture. Both decrease the fusion temperature from 2050°C to 950°C and make the mass good conductor of electricity.

#### Answers: Matching Type Questions

- [A] (a—iii); (b—i); (c—iv); (d—v); (e—ii)
- [B] (a—iii); (b—i); (c—v); (d—iv); (e—ii)
- [C] (a-v); (b-iii); (c-i); (d-ii); (e-iv)
- [D] (a-ii); (b-iii); (c-i); (d-v); (e-iv)

## ILLUSTRATIONS OF OBJECTIVE QUESTIONS



- 1. Correct match is:
  - (a) Ordinary form of borax

Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·5H<sub>2</sub>O

- (b) Colemanite
- Ca<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·5H<sub>2</sub>O
- (c) Boronatrocalcite
- 2Mg<sub>3</sub>B<sub>8</sub>O<sub>15</sub>·MgCl<sub>2</sub>
- (d) Octahedral form of borax:

Ans. (b)

- Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O
- 2. Which of the following is correct?
  - (a) The members of  $B_nH_{n+6}$  are less stable than  $B_nH_{n+4}$
  - (b) Diborane is coloured and unstable at room temperature
  - (c) The reaction of diborane with oxygen is endothermic
  - (d) All of the above

Ans. (a)

- 3. In which of the following, a salt of the type KMO2 is
  - (a)  $B_2H_6 + KOH(aq.) \longrightarrow$  (b)  $Al + KOH(aq.) \longrightarrow$
  - (c) Both

(d) None

Ans. (c)

[Hint: 
$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$$
;  
 $2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2$  +  $3H_2$ ]
Pot. metaaluminate

- 4. Which of the following minerals does not contain aluminium?
  - (a) Cryolite
- (b) Mica
- (c) Feldspar
- (d) Fluorspar

Ans. (d)

[Hint: Cryolite—Na<sub>3</sub>AlF<sub>6</sub>; Feldspar—KAlSi<sub>3</sub>O<sub>8</sub>; Mica — K<sub>2</sub>O·3Al<sub>2</sub>O<sub>3</sub>·6SiO<sub>2</sub>·2H<sub>2</sub>O; Fluorspar—CaF<sub>2</sub>]

- The function of fluorspar in the electrolytic reduction of alumina dissolved in fused cryolite (Na<sub>3</sub>AlF<sub>6</sub>) is :
  - (a) as a catalyst
  - (b) to lower the temperature of melt and to make the fused mixture very conducting
  - (c) to decrease the rate of oxidation of carbon anode
  - (d) none of the above

Ans. (b)

- 6. A layer of coke is spread over bauxite during electrolytic reduction of alumina by Hall - Heroult process. This layer acts as a/an:
  - (a) flux
  - (b) slag to remove impurities
  - (c) reducing agent
  - (d) insulation and does not allow heat to escape
- Which of the following compounds is formed in borax bead test? [A.I.I.M.S. 2004]
  - (a) Metaborate
- (b) Tetraborate
- (c) Double oxide
- (d) Orthoborate

[Hint: Borax on heating gives B<sub>2</sub>O<sub>3</sub> (transparent glassy mass). When hot B<sub>2</sub>O<sub>3</sub> is brought in contact with a coloured salt, metaborates are formed.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{-Heat} B_2O_3 \xrightarrow{Coloured} Metaborate$$

$$CuSO_4 + B_2O_3 \longrightarrow Cu(BO_2)_2 + SO_3$$

- 8. Aluminium chloride exists as a dimer, Al<sub>2</sub>Cl<sub>6</sub>, in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives: [A.I.E.E. 2004]
  - (a)  $Al^{3+} + 3Cl^{-}$
- (b)  $[Al(H_2O)_6]^{3+} + 3Cl^{-}$
- (c)  $[Al(OH)_6]^{3-} + 3HCl$
- (d)  $Al_2O_3 + 6HCl$

Ans. (b)

[Hint: The dimeric formula, Al<sub>2</sub>Cl<sub>6</sub>, is retained in non-polar solvent but is broken into [Al(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> on dissolution in water on account of high heat of hydration.]

- 9. Inorganic graphite is:
  - (a)  $B_3N_3H_6$
- (b)  $B_3N_3$

(c) SiC

(d)  $P_4S_3$ 

Ans. (b)

- 10. Hydrated AlCl<sub>3</sub> is used as:
  - (a) catalyst in cracking of petroleum
  - (b) catalyst in Friedel-Crafts reaction
  - (c) mordant
  - (d) all of the above

Ans. (c)

- 11. Borax is used as a cleansing agent because on dissolving in water, it gives: [A.I.I.M.S. 2006]
  - (a) alkaline solution
- (b) acidic solution
- (c) bleaching solution
- (d) neutral solution

Ans. (a)

[Hint: Borax dissolves in water and gives an alkaline solution.

Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> + 7H<sub>2</sub>O 
$$\Longrightarrow$$
 2NaOH + 4H<sub>3</sub>BO<sub>3</sub> ]  
Strong Weak acid

- **12.** Al<sub>2</sub>O<sub>3</sub> can be converted to anhydrous AlCl<sub>3</sub> by heating: [C.B.S.E. 2006]
  - (a) a mixture of Al<sub>2</sub>O<sub>3</sub> and carbon in dry Cl<sub>2</sub> gas
  - (b) Al<sub>2</sub>O<sub>3</sub> with Cl<sub>2</sub> gas
  - (c) Al<sub>2</sub>O<sub>3</sub> with HCl gas
  - (d) Al<sub>2</sub>O<sub>3</sub> with NaCl in solid state

Ans. (a)

[Hint:  $Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$ ]

- **13.** Boric acid is used in carrom boards for smooth gliding of pawns because:
  - (a) H<sub>3</sub>BO<sub>3</sub> molecules are loosely chemically bonded and hence soft
  - (b) its low density makes it fluffy
  - (c) it is chemically inert with the plywood
  - (d) H-bonding in  $H_3BO_3$  gives it a layered structure Ans. (d)
- 14. Boric acid is polymeric due to:
  - (a) its monobasic nature
  - (b) its acidic nature
  - (c) the presence of hydrogen bonds
  - (d) its geometry

Ans. (c)

15. The chemical formula of feldspar is:

[E.A.M.C.E.T. (Engg.) 2007]

- (a) KAlSi<sub>3</sub>O<sub>8</sub>
- (b)  $Na_3AlF_6$
- (c) NaAlO<sub>2</sub>
- (d)  $K_2SO_4\cdot Al_2(SO_4)_3\cdot 4Al(OH)_3$

Ans. (a)

**16.** The chief impurity present in red bauxite is:

[D.C.E. (Engg.) 2007]

(a) SiO<sub>2</sub>

- (b)  $Fe_2O_3$
- (c) K<sub>2</sub>SO<sub>4</sub> Ans. (b)
- (d) NaF

## **OBJECTIVE QUESTIONS**



## Set ${\bf I}$ : This set contains questions with one correct answer.

1.	The formula of corundum is:	12.	Which one is borax?	
	(a) $Al_2O_3$ $\Box$ (b) $Al_2O_3H_2O$ $\Box$		(a) $Na_2B_4O_7 \cdot 10H_2O$	
_	(c) $Al_2O_3 \cdot 2H_2O$ $\Box$ (d) $Al_2O_3 \cdot 3H_2O$ $\Box$		(c) $Ca_2B_6O_{11}.5H_2O$	
2.	Aluminium belongs to:	13.	The electrolytic reduction method for extraction of aluminis	um
	(a) s-block elements $\square$ (b) p-block elements $\square$	*	was discovered by:	
_	(c) $d$ -block elements $\square$ (d) $f$ -block elements $\square$		(a) Hoope	
3.	Aluminium forms:		(c) Baeyer	
	(a) electrovalent compounds only	14.	Cryolite is:	
	(b) covalent compounds only		(a) sodium fluoride	
	(c) electrovalent and covalent compounds both		(b) aluminium fluoride	
	(d) coordinate compounds only $\Box$		(c) sodium aluminium fluoride	
4.	Alumina is:		(d) none of the above	
	(a) acidic $\Box$ (b) basic $\Box$	15.	Which one of the following is not an ore of aluminium?	
	(c) neutral $\Box$ (d) amphoteric $\Box$	,	(a) Bauxite	
5.	The metal which evolves hydrogen, when treated with		(c) Epsomite	
	caustic soda solution is:	16.	When alumina is heated with carbon in nitrogen atmosphe	ere.
	(a) Cu		the products are:	
	(c) Ni $\square$ (d) Al $\square$		(a) $Al + CO$ $\Box$ (b) $Al + CO_2$	
6.	When aluminium is heated in atmosphere of nitrogen forms		(c) $Al + CO + CO_2$ $\Box$ (d) $AlN + CO$	
	a nitride of formula:	17.	When alumina is electrolysed in presence of cryolite, the	gas
	(a) AlN $\square$ (b) Al <sub>3</sub> N $\square$		liberated at graphite anode is:	U
	(c) $AlN_3$ $\Box$ (d) $Al_2N_3$ $\Box$		(a) $F_2$ $\Box$ (b) $O_2$	
7.	Which one of the following is most abundant in the earth's		(c) $CF_4$ $\Box$ (d) $F_2O$	
	crust?	18.	The electrolysis of pure alumina is not feasible because:	:
	(a) B		(a) it is bad conductor of electricity and its fusion temper	
^	(c) Ga		ture is high	
8.	The major role of fluorspar (CaF <sub>2</sub> ) which is added in small	,	(b) it is volatile in nature	
	quantity in the electrolytic reduction of alumina dissolved in		(c) it is decomposed when fused	
	fused cryolite, Na <sub>3</sub> AlF <sub>6</sub> , is:		(d) it is amphoteric	
	(i) as a catalyst	19.	In the extraction of aluminium, the function of cryolite is	to:
	(ii) to make the fused mixture very conducting		(a) lower the melting point of alumina	
	<ul><li>(iii) to lower the temperature of the melt</li><li>(iv) to decrease the rate of oxidation of carbon at the anode</li></ul>		(b) increase the melting point of alumina	
	(a) (i) and (ii)		(c) remove impurities from alumina	
	(c) (ii) and (iii) $\square$ (d) (i) and (iii) $\square$		(d) minimise the anodic effect	
Q	Al and Ga have nearly the same covalent radii because of:	20.	Aluminium does not react with:	
	(a) greater shielding effect of $s$ electrons of Ga atoms $\Box$		(a) NaOH	
	(b) poor shielding effect of $s$ electrons of Ga atoms $\square$		(c) $N_2$	
,	(c) poor shielding effect of $d$ electrons of Ga atoms $\Box$	21.	The common impurities present in bauxite ore are:	
	(d) greater shielding effect of $d$ electrons of Ga atoms $\Box$		(a) $Fe_2O_3$ and $CuO$ $\Box$ (b) $Fe_2O_3$ and $PbO$	
	Which of the following has the lowest melting point?		(c) $Fe_2O_3$ and $SiO_2$ $\Box$ (d) $SiO_2$ and $CuO$	
	(a) B	22.	In Hall's process, the ore is mixed with:	_
	(c) Al $\Box$ (d) Tl $\Box$		(a) coke	
11.	Which of the following is acidic in nature? [A.I.I.M.S. 2004]		(c) sodium hydroxide	
	(a) Be(OH) <sub>2</sub> $\square$ (b) Mg(OH) <sub>2</sub> $\square$	23.	Borax is prepared by treating colemanite with:	_
	(c) $AI(OH)_3$ $\Box$ (d) $B(OH)_3$ $\Box$		(a) NaNO <sub>3</sub>	
	[Hint: Mg(OH) <sub>2</sub> is a weak base and Be(OH) <sub>2</sub> and Al(OH) <sub>3</sub> are	- 24	(c) NaHCO <sub>3</sub>	
	amphoteric in nature. B(OH) <sub>3</sub> can accept one hydroxyl ion	24.	· · · · · · · · · · · · · · · · · · ·	1. <b>OT</b>
	from water and proton is released. Thus, it acts as a Lewis	1.	borax, the following compound is formed:	
•	acid.]		<ul> <li>(a) boron hydride</li> <li>(b) orthoboric acid</li> <li>(c) metaboric acid</li> <li>(d) pyroboric acid</li> </ul>	
	1		(c) metaboric acid	ш

25.	Which of the following compounds is formed when boron	n ·		Therefore, it should not be stored in glass or metal containers.]
	trichloride is treated with water?	,	38.	Which one of the following is a correct statement?
	(a) $H_3BO_3+HC1$	- 1	ا ا	[P.M.T. (M.P.) 1993]
26	(c) $B_2O_3 + HCl$ $\Box$ (d) None of these $\Box$		•	(a) The hydroxide of aluminium is more acidic than that of
26.	is the by-product obtained in the Serpek's process	_		boron
	(a) Oxygen	_		(b) The hydroxide of boron is basic while that of aluminium
27	(c) Nitrogen dioxide	ן נ		is amphoteric
27.	Aluminium metal is purified by:	.		(c) The hydroxide of boron is acidic while that of aluminium
	(a) Hoopes process			is amphoteric
20	(c) Serpek's process	-		(d) The hydroxides of both boron and aluminium are
28.	(a) It is bad conductor of electricity	ا -		amphoteric $\square$
	(a) It is bad conductor of electricity  (b) It is malleable and ductile		39.	$B(OH)_3 + NaOH \Longrightarrow Na[B(OH)_4]$
	(c) It is found free in nature			How can this reaction be made to proceed in forward
	(d) Alloys of aluminium are heavy			direction? [I.I.T. 2006]
29.	Which one of the following is not the alloy of aluminium?		} .	(a) Addition of $cis-1,2$ -diol
49.		_ ]		(b) Addition of borax
	.,	_ ]		(c) Addition of <i>trans</i> -1,2-diol □
30.	In the alumino-thermite process, Al acts as:	_		(d) Addition of $Na_2HPO_4$
50.		ם כ		[Hint: Na[B(OH) <sub>4</sub> ] is removed from the equilibrium due to the
	( )	_ 	,	formation of chelate compound with cis-1,2-diol and the
31.	Alumina may be converted into anhydrous aluminium			reaction moves in the forward direction.
J1.	chloride by:		CH	$H_2$ —OH $+$ $\begin{bmatrix} HO \\ HO \end{bmatrix}$ $\rightarrow$ $\begin{bmatrix} H_2C$ —O $\\ H_2C$ —O $\end{bmatrix}$ $\rightarrow$ $\begin{bmatrix} H_2C$ —O $\\ O$ — $CH_2 \end{bmatrix}$ $\begin{bmatrix} +4H_2O \end{bmatrix}$
	•	J	2	+ $+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$
		5	Cr	$H_2$ —OH [HO OH] [ $H_2$ C—O O—C $H_2$ ]
	·	5	40.	Colemanite is a mineral of:
٠	(d) mixing it with carbon and heating the mixture in a curren	nt		(a) Ca
		<u> </u>		(c) Al
32.	Which of the following statements about anhydrou	ıs	41.	The correct order of atomic radii of group 13 elements is:
	aluminium chloride is correct?			(a) $B < Al \sim Ga > In$
	(a) It exists as AlCl <sub>3</sub> molecule		<i>'</i>	(c) $B < Al < Ga \sim In$ $\square$ (d) $B < Ga < Al \sim In$ $\square$
	(b) It is a strong Lewis base		42.	When strongly heated, orthoboric acid leaves a residue of:
	(c) It sublimes at 100°C under vacuum	⊐.		(a) metaboric acid $\Box$ (b) tetraboric acid $\Box$
	(d) It is not easily hydrolysed	<b>_</b>		(c) boric anhydride $\Box$ (d) boron $\Box$
33.	Which hydroxide is soluble in sodium hydroxide?		43.	Boric acid is prepared from borax by the action of:
	(a) $Fe(OH)_3$	⊐		(a) hydrochloric acid $\Box$ (b) sodium hydroxide $\Box$
	(c) $Cr(OH)_3$			(c) carbon dioxide $\Box$ (d) sodium carbonate $\Box$
34.	The nature of the solution of potash alum is:		44.	When a solution of sodium hydroxide is added in excess to
				the solution of potash alum, we obtain:
	( )			(a) a white precipitate
35.	Which one of the following is alum?	٠.		(b) bluish white precipitate
-	(a) $NH_4Fe (SO_4)_2 \cdot 12H_2O$			(c) a clear solution
	(b) KCl·MgCl <sub>2</sub> ·6H <sub>2</sub> O		٠.٠	(d) a crystalline mass
	(c) $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$		45.	Borax bead test is responded by:
	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			(a) divalent metals
36.	Alums are used for:	_	1	(c) light metals
50.	·		1	(d) metals which form coloured metaborates
			46.	1
37.	The liquefied metal expanding on solidification is:			(a) no reaction takes place
٥,,	[A.I.I.M.S. 200	<u>.</u> 41		(b) oxygen is evolved
		ر <del>د</del> [		(c) water is produced
			477	(d) hydrogen is evolved
	[Hint: Ga is a soft silvery white metal and is liquid at roo		47.	, 5 5 6
	temperature. When it solidifies, it expands by 3.1 per cer			(a) isoelectronic
			1	(c) both (a) and (c) $\square$ (d) none of these $\square$

48.	When excess of NaOH solution is added in potash alum, the		11	_ _
	product is :		(=) Pressure stars	
	(a) A bluish precipitate $\Box$ (b) Clear solution $\Box$	57.	Which of the following is most acidic?	
	(c) A white precipitate $\Box$ (d) A greenish precipitate $\Box$		(a) $Na_2O$ $\square$ (b) $MgO$ $\square$	J
	[Hint: Alum consists Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> which reacts with NaOH.		(a) 14203	3
	$Al_2(SO_4)_3 + 6NaOH \longrightarrow 2Al(OH)_3 + 3Na_2SO_4$	58.	Al <sub>2</sub> O <sub>3</sub> formation from aluminium and oxygen involve	
	$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$		evolution of a large quantity of heat, which makes aluminium	n
	Soluble		use in:	
	The other sulphates K <sub>2</sub> SO <sub>4</sub> and Na <sub>2</sub> SO <sub>4</sub> are also soluble in	1	(a) deoxidiser $\Box$ (b) confectionary $\Box$	
	water. Thus, a clear solution is obtained.]		(c) indoor photography $\square$ (d) thermite welding $\square$	
49.	Three centred bond is present in:	59.	Anhydrous aluminium chloride is obtained when:	
	(a) $NH_3$ $\square$ (b) $B_2H_6$ $\square$		(a) aluminium oxide reacts with HCl	
	(c) $BCl_3$ $\Box$ (d) $AlCl_3$ $\Box$		(b) aluminium reacts with HCl	
50.	In diborane:		(c) aluminium is heated in a current of dry chlorine	
•	(a) 4 bridged hydrogens and two terminal hydrogens are	ļ	(d) aluminium hydroxide reacts with HCl	
	present	60.	Alum is used by dyers of cloth:	
	(b) 2 bridged hydrogens and four terminal hydrogens are		(a) for fire proofing fabrics	$\Box$
	present	1		
	(c) 3 bridged hydrogens and three terminal hydrogens are		(c) for softening hard water	
	present		<del>-</del>	
	(d) none of the above	61.	Aluminium chloride exists as a dimer because aluminium has	s:
51.		1		$\Box$
	containing washing soda since:			<u> </u>
	(a) washing soda reacts with aluminium to form soluble	62.		
	aluminate		with the evolution of much heat?	
	(b) washing soda is expensive			
	(c) washing soda is easily decomposed			
	(d) washing soda reacts with aluminium to form insoluble	63.	BCl <sub>3</sub> does not exist as a dimer but BH <sub>3</sub> exists as B <sub>2</sub> H	
	aluminium oxide		because:	-0
52.	Aluminium is more reactive than iron. But aluminium is less	1.	_	
	easily corroded than iron because:		(b) large size of chlorine atom does not fit between sma	
	(a) oxygen forms a protective oxide layer on aluminium $\Box$		sized boron atoms, while small sized hydrogen atom	
	(b) aluminium is a noble metal			
	(c) iron undergoes reaction easily with water			
	(d) iron forms mono and divalent ions			
53	Alumina is:	64.		
00.	(a) a bad conductor of electricity	0	· · · · · · · · · · · · · · · · · · ·	
	(b) a good conductor of electricity			
2	(c) a dehydrating agent	1		
	(d) soluble in water		* * * * * * * * * * * * * * * * * * *	
54.		65.	Thermite is a mixture of:	
J-1.	chloride.	00.	(a) 3 parts of powdered aluminium and 1 part of ferric oxid	de.
	(a) Friedel-Crafts reaction		(a) 5 parts of powdered adminimum and 1 part of ferrie oxic	
	(b) Cannizzaro reaction		(b) 1 part of powdered aluminium and 3 parts of ferric oxid	 -}_
	(c) Kolbe's reaction		(b) I part of powdered aluminium and 3 parts of terric oxic	
	(d) Hofmann's reaction		(c) 1 part of powdered aluminium and 1 part of ferric oxid	اب اما
55	Alumina is not used as:		(c) I part of powdered aluminium and I part of lettic oxid	
JJ.	(a) refractory material		(d) 2 parts of powdered aluminium and 3 parts of ferric oxid	 -1_0
			_ · · · · · · · · · · · · · · · · · · ·	
		66	•	
		66.	The most covalent aluminium halide is:	_
56	(a) 11,11111 F.S.111111		(7)	
56.	•	(7	(-)	
	semi-precious stone is a mineral of the following class:	67.	,	.ie
	(a) sodium alumino silicate		chemical used is:	_
	(b) zinc cobaltate	1	(a) Na <sub>2</sub> CO <sub>3</sub>	Ш

	(b) cryolite		80.	In $B_2H_6$ :	
	(c) NaOH			(a) there is direct boron-boron bond	
	(d) a mixture of NaOH and Na <sub>2</sub> CO <sub>3</sub>			(b) the boron atoms are linked through hydrogen bridges	ŀ
68.	When aluminium is heated with conc. H <sub>2</sub> SO <sub>4</sub> :				
	(a) aluminium becomes passive			(c) the structure is similar to $C_2H_6$	
	(b) hydrogen is liberated				
	(c) oxygen is liberated		81.	The colour of ferric metaborate is:	
	(d) sulphur dioxide is liberated			(a) yellow	
69.	When aluminium hydroxide dissolves in NaOH solution	, the			
	product is:		82.	Thermite is a mixture of iron oxide and:	
	(a) $[Al(H_2O)_3(OH)_3]$			(a) Al powder	
	(a) $[Al(H_2O)_3(OH)_3]$			(c) K metal	
70.	Which one of the following statements regarding BF <sub>3</sub> is	s not	83.	Inorganic graphite is:	
	correct?		)	(a) $B_3N_3H_6$	
•	(a) It is a Lewis acid			( )	
	(b) It is an ionic compound		84.		
	(c) It is an electron deficient compound		'		
	(d) It forms adducts			— · (-)g	
71.	Which one is not a borane?		85.	LiAlH <sub>4</sub> is obtained by reacting an excess of with a	an
	(a) $B_5H_9$			ethereal solution of AlCl <sub>3</sub> .	
	(c) $B_5H_{11}$			(a) LiH	
	[Hint: General formulae of boranes are $B_nH_{n+4}$ and $B_nH$	6.]	0.5	(-)	
72.	In which of the following elements +1 oxidation state is a		86.	Boron compounds behave as Lewis acids because of the	Iľ:
	stable than +3?			(a) acidic nature	
	(a) B $\square$ (b) Al		}		
	(c) Ga				
73.	Boron nitride is isoelectronic with:		97	(d) electron deficient nature Aluminium (III) chloride forms a dimer because aluminium	
	(a) $C_2$ $\Box$ (b) $B_2$		07.		ı.
	(c) $N_2$ $\square$ (d) $O_2$				
74.	The number of OH units directly linked to boron atom	ns in	1		
	$Na_2B_4O_7 \cdot 10H_2O$ is:				
	(a) 2		88.	Which one of the following statements about H <sub>3</sub> BO <sub>3</sub> is n	ot
	(c) 4			correct?	
75.	From B <sub>2</sub> H <sub>6</sub> , all the following can be prepared except:			(a) It is a strong tribasic acid	
	(a) $B_2O_3$ $\Box$ (b) $H_3BO_3$			(b) It is prepared by acidifying an aqueous solution of bord	ax
	(c) $B_2(CH_3)_6$ $\Box$ (d) $NaBH_4$				
76.	The halides of group IIIA elements behave as Lewis a	cids.		(c) It has a layer structure in which planar BO <sub>3</sub> units a	ıre
	The acceptor ability is maximum for the halides of:			joined by hydrogen bonds	Ц
	(a) Tl			(d) It does not act as proton donor as it acts as a Lewis ac	br
	(c) Al		- 00	by accepting hydroxyl ions	П
77.	The power of halides of boron to act as Lewis		89.	C	m
	decreases in the order: [C.B.S.E. (P.M.T.) Prel.				
	(a) $BF_3 > BCl_3 > BBr_3$	Ц	90.		
70	(c) $BCl_3 > BF_3 > BBr_3$ $\square$ (d) $BCl_3 > BBr_3 > BF_3$		1 70.	of diborane is concerned:	110
78.	Silicon shows similarities with:			(a) There are two bridging hydrogen atoms in diborane	
	(a) aluminium			(b) Each boron atom forms four bonds in diborane	
70	(c) boron	- 🗆		(c) The hydrogen atoms are not in the same plane	in
79.	Which of the following is a false statement?			***	
	<ul><li>(a) BH<sub>3</sub> is not a stable compound</li><li>(b) Boron hydrides are formed when dil. HCl reacts</li></ul>			(d) All B—H bonds in diborane are similar	
,		Willi	. 91.	Which of the following processes does not involve	a
	$Mg_3B_2$ (c) All the B—H bond distances in $B_2H_6$ are equal			catalyst?	
	(d) The boron hydrides are readily hydrolysed			1	
	(w) (1119) DOI OH HYDRIGOD MC TOMMY HYDROLY OCC	· ·	1	(c) Contact process	П

92.	AlCl <sub>3</sub> on hydrolysis gives:		(a) Glycerol $\Box$ (b) Acetic acid $\Box$
	(a) $Al_2O_3 \cdot H_2O$ $\square$ (b) $Al(OH)_3$ $\square$	١,	(c) Ethyl alcohol $\Box$ (d) Ethylene $\Box$
	(c) $Al_2O_3$ $\Box$ (d) $AlCl_3 6H_2O$ $\Box$	102.	Specify the coordination geometry around and hybridiza-
93.	Thallium shows different oxidation states because:		tion of N and B atoms in 1:1 complex of BF <sub>3</sub> and NH <sub>3</sub> :
	(a) of its high reactivity $\Box$		[I.I.T. (S) 2002]
	(b) of inert pair of electrons	ĺ.	(a) N: tetrahedral, $sp^3$ ; B: tetrahedral, $sp^3$
	(c) of its amphoteric nature	)	(b) N : pyramidal, $sp^3$ ; B : pyramidal, $sp^3$
	(d) it is a transition metal		(c) N : pyramidal, $sp^3$ ; B : planar, $sp^3$
94.	In the commercial electrochemical process for aluminium	{	(d) N : pyramidal, $sp^3$ ; B : tetrahedral, $sp^3$
	extraction, the electrolyte used is:	103.	
	(a) Al(OH) <sub>3</sub> in NaOH solution	103.	
	(b) an aqueous solution of $Al_2(SO_4)_3$	 	(a) monobasic and weak Lewis acid
	(c) a molten mixture of Al <sub>2</sub> O <sub>3</sub> and Na <sub>3</sub> AlF <sub>6</sub>	[	(b) monobasic and weak Bronsted acid
	(d) a molten mixture of AlO(OH) and Al(OH) <sub>3</sub>		(c) monobasic acid and strong Lewis acid
95.	Electrolytic reduction of alumina to aluminium by Hall-	104	(d) tribasic acid and weak Bronsted acid
,,,	Heroult process is carried out: [I.I.T. (S) 2000]	104.	Which of the following compounds is known as inorganic
	(a) in presence of NaCl	ļ	benzene? [P.M.E.T. 2003]
	(b) in presence of fluorite	l .	(a) $B_6H_6$ $\Box$ (b) $C_5H_5B$ $\Box$
	(c) in the presence of cryolite which forms a melt with lower		(c) $C_3N_3H_3$ $\square$ (d) $B_3N_3H_6$ $\square$
	melting temperature	105.	Which one of the following is the correct statement?
	(d) in the presence of cryolite which forms a melt with the	100.	[A.I.E.E. 2008]
	higher melting temperature	ļ	(a) $B_2H_6 \cdot 2NH_3$ is known as 'inorganic benzene'
96.	Aluminium oxide is not reduced by chemical reactions		(b) Boric acid is a protonic acid
<i>5</i> 0.	since: [K.C.E.T. 2002]		(c) Beryllium exhibits coordination number of six
	(a) aluminium oxide is highly stable	Ì	
	(b) aluminium oxide is stable	}	(d) Chlorides of both beryllium and aluminium have bridged
	(c) reducing agent contaminates		chloride structures in solid phase
		106.	The ion(s) that act/s as oxidising agent in solution is/are:
97.	(-) P P		[P.M.T. (Kerala) 2008]
91.		1	(a) Te <sup>+</sup> and Al <sup>3+</sup> $\square$ (b) B <sup>3+</sup> and Al <sup>3+</sup> $\square$
			(c) $Te^{3+}$ only $\Box$ (d) $B^{3+}$ only $\Box$
	_ (-),	107.	H <sub>3</sub> PO <sub>3</sub> has nonionisable P—H bonds:
00	(e) iron	107.	
98.		1	[J.E.E. (Orissa) 2008] (a) none
	aluminium. This acts as a/an: [P.M.T. (Manipal) 2002]	1	(a) Holle $\Box$ (b) 1 $\Box$ (c) 2 $\Box$ (d) 3 $\Box$
	(a) flux	108	
	(b) slag to remove impurities	100	The chemical formula of feldspar is: [P.M.T. (Punjab) 2008]
	(c) reducing agent		(a) $KAlSi_3O_8$
00	(d) insulation and does not allow heat to escape		(b) $Na_3AlF_6$
99.	Alum helps in purifying water by: [A.I.E.E.E. 2002]	ļ.	(c) NaAlO <sub>2</sub>
	(a) forming Si complex with clay particles	·	(d) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$
	(b) sulphate part which combines with the dirt and	109.	Which of the following is not correct? [C.P.M.T. 2008]
	removes it	10).	(a) Al reacts with NaOH and liberates $H_2$
	(c) aluminium which coagulates the mud particles		(b) AlCl <sub>3</sub> is a Lewis acid
100	(d) making the mud, water soluble	j	(c) Al is used in the manufacture of electrical cables
100.		· ·	(d) NaOH is used during Hall's process of purification of
	to its: [C.E.E. (Kerala) 2002]	} .	bauxite
	(a) strong reducing nature	110.	Boron halides behave as Lewis acids because of their
	(b) weak reducing action	1	·
	(c) strong Lewis acid nature	110.	nature: [E.A.M.C.E.T. (Engg.) 2008]
	(c) strong Lewis acid nature (d) weak Lewis acid character		nature: [E.A.M.C.E.T. (Engg.) 2008] (a) proton donor $\square$ (b) covalent $\square$
101.	(c) strong Lewis acid nature  (d) weak Lewis acid character  Boric acid is a very weak acid but in presence of certain		nature: [E.A.M.C.E.T. (Engg.) 2008] (a) proton donor $\square$ (b) covalent $\square$ (c) electron deficient $\square$ (d) ionising $\square$
101.	(c) strong Lewis acid nature  (d) weak Lewis acid character  Boric acid is a very weak acid but in presence of certain organic compounds, it acts as a strong acid. Which one of	111.	nature: [E.A.M.C.E.T. (Engg.) 2008]  (a) proton donor □ (b) covalent □  (c) electron deficient □ (d) ionising □  A mixture of boron trichloride and hydrogen is subjected
101.	(c) strong Lewis acid nature  (d) weak Lewis acid character  Boric acid is a very weak acid but in presence of certain organic compounds, it acts as a strong acid. Which one of the following organic compounds can affect such change?		nature: [E.A.M.C.E.T. (Engg.) 2008]  (a) proton donor
101.	(c) strong Lewis acid nature  (d) weak Lewis acid character  Boric acid is a very weak acid but in presence of certain organic compounds, it acts as a strong acid. Which one of		nature: [E.A.M.C.E.T. (Engg.) 2008]  (a) proton donor □ (b) covalent □  (c) electron deficient □ (d) ionising □  A mixture of boron trichloride and hydrogen is subjected

112. 113.	(a) $H_3BO_3$	•	Which one of the following molecular hydrides acts as a Lewis acid? [C.B.S.E. (P.M.T.) 2010]  (a) $NH_3$
	Al <sub>2</sub> O <sub>3</sub> (s) + 2OH <sup>-</sup> (aq) $\longrightarrow$ 2AlO <sub>2</sub> (aq) + H <sub>2</sub> O(l) Solid impurities such as Fe <sub>2</sub> O <sub>3</sub> and SiO <sub>2</sub> are removed and then Al(OH) <sub>3</sub> is reprecipitated.  2Al(OH) <sub>4</sub> $\longrightarrow$ Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O(s) + 2OH <sup>-</sup> (aq)  In the industrial world:  [J.E.E. (W.B.) 2009]  (a) carbon dioxide is added to precipitate the alumina $\square$ (b) temperature and pressure are dropped and the super saturated solution seeded $\square$ (c) both (a) and (b) are practised	117.	[A.M.U. (Engg.) 2010] (a) $TiO_2 + 4Na \longrightarrow Ti + 2Na_2O$ (b) $2A1 + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$ (c) $SnO_2 + 2C \longrightarrow Sn + 2CO$ (d) $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$
•	(d) the water is evaporated $\Box$ II: This set contains questions with two or more corrections	ect ans	
118. 119.	Which of the following oxides are basic?  (a) $B_2O_3$ $\square$ (b) $Tl_2O$ $\square$ (c) $In_2O_3$ $\square$ (d) $Al_2O_3$ $\square$ Stability of monovalent and trivalent cations of Ga, In, TI lie in following sequence:  (a) $Ga^{3+} < In^{3+} > Tl^{3+}$ $\square$ (b) $Ga^{3+} > In^{3+} > Tl^{3+}$ $\square$ (c) $Tl^+ > In^+ > Ga^+$ $\square$ (d) $Ga^{3+} > In^+ > Tl^+$ $\square$ Which of the following elements do not form carbide?	125.	(a) a white gelatinous precipitate (b) insoluble in excess of NH <sub>4</sub> OH (c) soluble in excess of NaOH (d) amphoteric in nature  Which of the following metals are extracted by using Al as a reducing agent? (a) Na from Na <sub>2</sub> O  □ (b) Cr from Cr <sub>2</sub> O <sub>3</sub> □ (c) W from WO <sub>3</sub> □ (d) Mg from MgO  Aluminium becomes possive in
121. 122.	(a) B □ (b) Al □ C In □ (d) Ga □ C In □ (d) Ga □ C In □ (d) Ga □ C In □ (d) BO <sub>2</sub> ) differ in respect of:  (a) basicity □ (b) structure □ C In melting point □ (d) oxidation □ C In Select the correct statements about diborane:	126. 127.	Aluminium becomes passive in:  (a) conc. HNO <sub>3</sub>
123.	(a) $B_2H_6$ has three centred bond  (b) Each boron atom lies in $sp^3$ hybrid state  (c) $H_b \dots B \dots H_b$ bond angle is 122°  (d) All hydrogens in $B_2H_6$ lie in the same plane  Possible oxidation states of boron family elements are:	128.	<ul> <li>(c) It has a layer structure in which BO<sub>3</sub> units are joined by hydrogen bonds □</li> <li>(d) It is obtained by treating borax with conc. H<sub>2</sub>SO<sub>4</sub> □</li> <li>In the reaction 2X + B<sub>2</sub>H<sub>6</sub> → [BH<sub>2</sub>X<sub>2</sub>]<sup>+</sup>[BH<sub>4</sub>]<sup>-</sup></li> </ul>
	(a) +1 $\square$ (b) +2 $\square$ (c) +3 $\square$ (d) +4 $\square$ $Al_2(SO_4)_3 + NH_4OH \longrightarrow X. X is:$		the amine(s) $X$ is (are):  [I.I.T. 2009]  (a) NH <sub>3</sub> $\Box$ (b) CH <sub>3</sub> NH <sub>2</sub> $\Box$ (c) (CH <sub>3</sub> ) <sub>2</sub> NH $\Box$ (d) (CH <sub>3</sub> ) <sub>3</sub> N $\Box$ [Hint: With (CH <sub>3</sub> ) <sub>3</sub> N, B <sub>2</sub> H <sub>6</sub> forms an adduct, (CH <sub>3</sub> ) <sub>3</sub> N $\rightarrow$ BH <sub>3</sub> ]

Ans	wer	4				-												
<b>1.</b> (a)	2.	(b)	3.	(c)	4.	(d)	5.	(d)	6.	(a)	7.	(b)	8.	(c)	9.	(c)	10.	(b)
<b>11.</b> (d)	12.	(a)	13.	(b)	14.	(c)	15.	(c)	16.	(d).	17.	(b)	18.	(a)	19.	(a)	20.	(d)
<b>21.</b> (c)	22.	(d)	23.	(d)	24.	(b)	25.	(a)	26.	(b)	27.	(a)	28.	(b)	29.	(c)	30.	(d)
<b>31.</b> (d)	32.	(c)	33.	(b)	34.	(a)	35.	(a)	36.	(d)	37.	(b)	38.	(c)	39.	(a)	40.	(b)
<b>41.</b> (a)	42.	(c)	43.	(a)	44.	(c)	45.	(d)	46.	(d)	47.	(b)	48.	(b)	49.	(b)	50.	(b)
<b>51.</b> (a)	52.	(a)	53.	(a)	54.	(a)	55.	(d)	56.	(a)	57.	(c)	58.	(d)	59.	(c)	60.	(d)
<b>61.</b> (b)	62.	(d)	63.	(b)	64.	(c)	65.	(b)	66.	(d)	67.	(c)	68.	(d)	69.	(c)	70.	(b)
<b>71.</b> (b)	72.	(d)	73.	(a)	74.	(c)	75.	(c)	76.	(d)	77.	(b)	78.	(c)	79.	(c)	80.	(b)
<b>81.</b> (a)	82.	(a)	83.	(c)	84.	(c)	85.	(a)	86.	(d)	87.	(d)	88.	(a)	89.	(d)	90.	(d)
<b>91.</b> (a)	92.	(b)	93.	(b)	94.	(c)	95.	(c)	96.	(a)	97.	(c)	98.	(d)	99.	(c)	100.	(c)
<b>101.</b> (a)	102.	(a)	103.	(a)	104.	(d)	105.	(d)	106.	(c)	107.	(b)	108.	(a)	109.	(d)	110.	(c)
<b>111.</b> (d)	112.	(d)	113.	(c)	114.	(c)	115.	(c)	116.	(b)	117.	(b)	118.	(b, c)	119.	(b, c)	120.	(c, d).
121. (a, b,	c)122.	(a, b, c)	123.	(a, c)	124.	(a,b,c,d)	125.	(b, c)	126.	(a,b,c)	127.	(a,b,c,d)	128.	(a,b,c)				



## Objective Questions for IIT ASPIRANTS



1.  $H_3BO_3 \xrightarrow{100^{\circ}C} X \xrightarrow{160^{\circ}C} Y \xrightarrow{\text{Red hot}} B_2O_3$ ;

X and Y respectively are:

- (a) X = Metaboric acid; Y = Tetraboric acid
- (b) X = Borax; Y = Metaboric acid
- (c) X = Tetraboric acid; Y = Metaboric acid
- (d) X = Tetraboric acid; Y = Borax

[Hint :H<sub>3</sub>BO<sub>3</sub>  $\xrightarrow{100^{\circ}\text{C}}$  HBO<sub>2</sub> (Metaboric acid) ; 4 HBO<sub>2</sub>  $\xrightarrow{160^{\circ}\text{C}}$   $\xrightarrow{(X)}$ 

H<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (Tetraboric acid)]

- Which one of the following compounds does not exist?
  - (a)  $B_2H_4(CH_3)_2$
- (b)  $B_2H_3(CH_3)_3$
- (c)  $B_2H_2(CH_3)_4$
- (d)  $B_2H(CH_3)_5$

[Hint: Not more than four hydrogen atoms can be substituted by methyl groups in the molecule of B2H6. The bridge hydrogen atoms are not to be substituted.]

- A gas other than HCl is obtained in:
  - (a)  $BCl_3 + H_2 \xrightarrow{\text{Silent electric}}$  (b)  $LiAlH_4 + BF_3$

(d) none of these

[Hint:  $2BCl_3 + 6H_2 \xrightarrow{\text{Silent electric}} B_2H_6 + 6HCl$ ;

 $3\text{LiAlH}_4 + 4\text{BF}_3 \xrightarrow{\text{Ether}} 2\text{B}_2\text{H}_6 + 3\text{LiF} + 3\text{AlF}_3$ (Gas)

- 4. AlCl<sub>3</sub> is an electron deficient compound but AlF<sub>3</sub> is not. This is because:
  - (a) atomic size of F is smaller than Cl which makes AlF<sub>3</sub> more
  - (b) AlCl<sub>3</sub> is a covalent compound while AlF<sub>3</sub> is an ionic compound
  - (c) AlCl<sub>3</sub> exists as a dimer but AlF<sub>3</sub> does not
  - (d) Al in AlCl<sub>3</sub> is in  $sp^3$  hybrid state but Al in AlF<sub>3</sub> is in  $sp^2$
- 5. Hydride of boron occurs as B<sub>2</sub>H<sub>6</sub> but B<sub>2</sub>Cl<sub>6</sub> does not exist. This is because:
  - (a)  $p\pi$ — $d\pi$  back bonding is possible in  $B_2H_6$  but not in  $B_2Cl_6$
  - (b) boron and hydrogen have almost equal values of electronegativity
  - (c) boron and chlorine have almost equal atomic sizes
  - (d) small hydrogen atoms can easily fit in between boron atoms but large chlorine atoms do not
- **6.** Bauxite ore is generally contaminated with impurity of oxides of two elements  $E_1$  and  $E_2$ . Which of the following statements is correct?
  - (a)  $E_1$  is a non-metal and belongs to 3rd period while  $E_2$  is a metal and belong to fourth period
  - (b) One of the two oxides has three dimensional polymeric structure
  - (c) Both (a) and (b) are correct
  - (d) None of the above

- [Hint: Two oxides present in bauxite as impurity are SiO2 and Fe<sub>2</sub>O<sub>3</sub>. Si belongs to 3rd period and Fe belongs to IVth period. SiO<sub>2</sub> has three dimensional structure.]
- 7. When an inorganic compound (X) having 3C-2e as well as 2e-2e bonds reacts with ammonia gas at a certain temperature, gives a compound (Y), isostructural with benzene. Compound (X) with ammonia at a high temperature produces a substance (Z).
  - (a) (X) is  $B_2H_6$
  - (b) (Z) is known as inorganic graphite
  - (c) (Y) is  $B_3N_3H_6$
  - (d) (Z) is soft like graphite

[Hint: Diborane, B2H6, is a compound consisting 3C-2e and

2e-2e bonds.  $B_2H_6 + 2NH_3 \xrightarrow{Low \text{ temp.}} B_2H_6 \cdot 2NH_3$  $\xrightarrow{200^{\circ}\text{C}}$  B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>. (Y) has structure similar to benzene. It is called inorganic benzene.  $B_2H_6 + NH_3 \xrightarrow{\text{High temp.}} (BN)_X$ .

(Z) is a hard substance.]

- Gallium has smaller atomic radius than aluminium because
  - (a) poor shielding power of d electrons of Ga atom
  - (b) poor shielding power of s electrons of Ga atom
  - (c) greater shielding power of s electrons of Al atom
  - (d) greater shielding power of d electrons of Ga atom
- 9. Boron does not form B<sup>3+</sup> cation easily. It is due to:
  - (a) energy required to form B<sup>3+</sup> ion is very high which will not be compensated by lattice energies or hydration energies of such ion
  - (b) boron is non-metal
  - (c) boron is semi-metal
  - (d) none of the above
- 10. Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O is correctly represented as:
  - (a)  $2NaBO_2 \cdot Na_2B_2O_3 \cdot 10H_2O$  (b)  $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$
  - (c)  $Na_2[B_4(H_2O)_4O_7] \cdot 6H_2O$  (d) all of the above

[Hint: Borax molecule is actually made of two tetrahedra and two triangular units joined as shown below.]

Na<sub>2</sub> HO—B O—B—OH ]

- 11. Orthoboric acid behaves as a weak monobasic acid giving  $H_3O^+$  and :
  - (a)  $[B(OH)_4]^+$
- (c)  $[B(OH)_4]^-$
- (d)  $H_2BO_2$

[Hint:  $B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$ ]

#### 12. Amorphous boron is extracted from borax by following steps:

Borax 
$$\xrightarrow{(A)}$$
 H<sub>3</sub>BO<sub>3</sub>  $\xrightarrow{\text{Heat}}$  B<sub>2</sub>O<sub>3</sub>  $\xrightarrow{(B)}$  Boron.

- (A) and (B) are:
- (a) H<sub>2</sub>SO<sub>4</sub>, Al
- (b) HCl, carbon
- (c) H<sub>2</sub>SO<sub>4</sub>, Mg
- (d) HCl, Fe

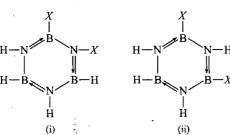
[Hint: 
$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$
;  
 $2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$ ;  
 $B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$ ]

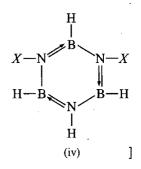
- 13. Aqueous solution of borax acts as a buffer because :
  - (a) it contains weak acid and its salt with strong base
  - (b) it contains tribasic acid and strong base
  - (c) it contains number of neutral water molecules
  - (d) none of the above

[Hint: 
$$Na_2B_4O_7 + 7H_2O \longrightarrow 2Na$$
 [B(OH)<sub>4</sub>] +  $2H_3BO_3$ ]
Salt with strong Weak acid

- 14. General formula of aluminium alums is:
  - (a)  $[M(H_2O)_6][Al(H_2O)_6][SO_4]_3$
  - (b)  $[M(H_2O)_4][Al(H_2O)_4][SO_4]_4$
  - (c)  $[M(H_2O)_4][Al(H_2O)_6][SO_4]_2$
  - (d)  $[M(H_2O)_6][Al(H_2O)_6][SO_4]_2$
- 15. The number of isomers possible for disubstituted borazine,  $B_3N_3H_4X_2$  is:
  - (a) 3
- (b) 4
- (c) 6
- (d) 5

[Hint:





Which of the statement is true for the above sequence of reactions?

- (a) Z is hydrogen
- (b) X is  $B_2H_6$
- (c) Z and Y are F<sub>2</sub> and B<sub>2</sub>H<sub>6</sub> respectively.
- (d) Z is potassium hydroxide

$$\begin{array}{ccc}
B + F_2 & \longrightarrow BF_3 \\
(Z) & (X)
\end{array}$$

$$\begin{array}{ccc} B+F_2 & \longrightarrow BF_3 & ; \\ (Z) & (X) & \\ 8BF_3+6LiH & \longrightarrow B_2H_6 + 6LiBF_4 \,] \end{array}$$

- 17. The structure of diborane (B<sub>2</sub>H<sub>6</sub>) contains: [ALE.E.E. 2005]
  - (a) four 2c-2e bonds and two 3c-2e bonds
  - (b) two 2c-2e bonds and four 3c-2e bonds
  - (c) two 2c-2e bonds and two 3c-3e bonds
  - (d) four 2c-2e bonds and four 3c-2e bonds

## ıswers

- 1. (a) 13. (a)
- 2. (d) 14. (d)
- 3. (c) 15. (b)
- 4. (b) 16. (c)
- 5. (d) 17. (a)
- 6. (c)
- 7. (a,b,c)
- 8. (a)
- **9.** (a)
- 10. (b)
- 11. (c) 12. (c)

## Assertion-Reason Type Questions

In each of the following questions two statements are given as Assertion (A) and Reason (R). Of the statements, mark the correct answer as:

- (a) If both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) If (A) is true but (R) is false.
- (d) If both (A) and (R) are false.
- (e) If (A) is false but (R) is true.

- 1. (A) Borax bead test is not suitable for Al (III).
  - (R) Al<sub>2</sub>O<sub>3</sub> is insoluble in water.
- 2. (A) Thallium exhibits oxidation states of +1 and +3.
  - (R) Thallium exhibits inert pair effect.
- 3. (A) Boric acid is a tribasic acid.
  - (R) Boric acid contains three hydroxyl groups.
- 4. (A) BF<sub>3</sub> is a weaker Lewis acid than BCl<sub>3</sub>.
  - (R) BF<sub>3</sub> molecule is stabilized to a greater extent than BCl<sub>3</sub> by B—F  $\pi$ -bonding.

- 5. (A) AlCl<sub>3</sub> forms dimer Al<sub>2</sub>Cl<sub>6</sub> but it dissolves in water forming [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> and Cl<sup>-</sup> ions.
  - (R) Aqueous solution of AlCl<sub>3</sub> is acidic due to hydrolysis.
- 6. (A) Aluminium is used as a reducing agent in thermite process.
  - (R) Aluminium can reduce Na<sub>2</sub>O to sodium.

- 7. (A) In water, orthoboric acid behaves as a weak monobasic acid.
  - (R) In water, orthoboric acid acts as a proton donor.

[LLT. 2007]

- (A) Boron always forms covalent bond.
  - The small size of B<sup>3+</sup> favours formation of covalent bond. [LI.T. 2007]

#### uswers 1. (b) 2. (a) 3. (e) **4.** (a) 5. (b) 6. (c) 7. (c) 8. (a)

# THOUGHT TYPE QUESTIONS

#### THOUGHT 1

Aluminium is stable in air and water inspite of the fact that it is reactive metal. The reason is that a thin film of its oxide is formed on its surface which makes it passive for further attack. The layer is so useful that in industry, it is purposely deposited by an electrolytic process called anodising.

Reaction of aluminium with oxygen is highly exothermic and is called thermite reaction.

$$2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s); \qquad \Delta H = -1670 \text{ kJ}$$

Thermite reaction finds applications in the metallurgical extraction of many metals from their oxides and for welding of metals. The drawback is that to start the reaction, high temperature is required for which an ignition mixture is used.

- 1. Anodising can be done by electrolysing dilute H<sub>2</sub>SO<sub>4</sub> with aluminium as anode. This results in:
  - (a) the formation of  $Al_2(SO_4)_3$  on the surface of aluminium
  - (b) the formation of oxide film (Al<sub>2</sub>O<sub>3</sub>) on the surface of aluminium anode
  - (c) the formation of polymeric aluminium hydride film on the surface of aluminium anode
  - (d) none of the above
- 2. The reaction which is not involved in thermite process:
  - $3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$
  - $Cr_2O_3+2Al \longrightarrow 2Cr + Al_2O_3$ (b)
  - $2Fe + Al_2O_3 \longrightarrow Fe_2O_3 + 2Al$ (c)
  - $B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3$
- 3. Thermite a mixture used for welding is:
  - (a) Fe and Al
    - (b) BaO and Mg powder
  - (c) Cu and Al (d) Fe<sub>2</sub>O<sub>3</sub> and Al powder
- 4. Anodised aluminium is:
  - (a) Al obtained at anode
  - (b) Al prepared electrolytically
  - (c) alloy of Al containing 95% Al
  - (d) Al electrolytically coated with aluminium oxide

- 5. Which one of the following metals cannot be extracted by using Al as a reducing agent?
  - (a) Na from Na<sub>2</sub>O
- (b) Cr from Cr<sub>2</sub>O<sub>3</sub>
- (c) W from WO<sub>3</sub>
- (d) Mn from Mn<sub>3</sub>O<sub>4</sub>
- Aluminium becomes passive in:
  - (a) conc. HNO<sub>3</sub>
- (b) H<sub>2</sub>CrO<sub>4</sub>
- (c) HClO<sub>4</sub>
- (d) all of these

THOUGHT 2
$$Ca_{2}B_{6}O_{11} + Na_{2}CO_{3} \xrightarrow{\text{Fused}} (A) + (B) + CaCO_{3}$$

$$(A) + CO_{2} \longrightarrow (B) + Na_{2}CO_{3}$$
Solution
$$(B) + \text{Conc. HCl} \longrightarrow \text{NaCl} + \text{Acid}$$

$$(C) \xrightarrow{\text{Strongly}} (D) \qquad \text{Acid } (C)$$

- (D) + CuSO<sub>4</sub>  $\xrightarrow{\text{Heated}}$  Blue coloured (E) compound
- 1. Compound (A) is:
  - (a) NaBO<sub>2</sub>
- (b) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>
- (c) Na<sub>3</sub>BO<sub>3</sub>
- (d) NaOH
- **2.** Compound (*B*) is :
  - (a) NaBO<sub>2</sub>
- (b)  $Na_2B_4O_7$
- (c) Na<sub>3</sub>BO<sub>3</sub>
- (d) NaOH
- 3. Compound (C) is:
  - (a)  $H_2B_4O_7$
- (b) HBO<sub>2</sub>
- (c)  $H_3BO_3$
- (d) HB<sub>3</sub>O<sub>5</sub>
- **4.** Compound (D) is:
  - (a) H<sub>3</sub>BO<sub>3</sub>
- (b)  $B_2O_3$

(c) B

- (d) none of these
- **5.** Compound (E) is:
  - (a) Cu<sub>2</sub>O
- (b) CuS
- (c) CuSO<sub>3</sub>
- (d)  $Cu(BO_2)_2$

## THOUGHT 3

(i) Boron + 
$$O_2 \xrightarrow{700^{\circ}C} (X)$$

(ii) 
$$(X) + C$$
 (carbon) +  $Cl_2 \longrightarrow (Y) + CO$ 

(iii) 
$$(Y)$$
 + LiAlH<sub>4</sub>  $\longrightarrow$   $(Z)$  + LiCl + AlCl<sub>3</sub>

$$(iv)(Z) + NH_3 \longrightarrow (A) \xrightarrow{Heat} (B)$$

(v) (Z) + NaH 
$$\longrightarrow$$
 (D)

- 1. Compound (Z) is:
  - (a) an ionic compound
  - (b) an electron deficient compound
  - (c) 3C—2e compound
  - (d) having ethane like structure
- Compounds (X) and (Y) are:

(a) 
$$(V) = PO$$
  $(V) = PC$ 

(a) 
$$(X) = BO_2$$
,  $(Y) = BCl_2$  (b)  $(X) = BO_3$ ,  $(Y) = BCl_4$ 

(c) 
$$(X) = B_2O_3$$
,  $(Y) = BCl_3$  (d)  $(X) = BO_3$ ,  $(Y) = B_4C$ 

(d) 
$$(X) = BO_3$$
,  $(Y) = B_4C$ 

- **3.** Compound (*B*) is :

  - (a) borazole (b) inorganic benzene
  - (c) borazon
- (d) boron nitride
- Compound (D) is used as a/an:
  - (a) oxidising agent
- (b) complexing agent
- (c) buffer agent
- (d) reducing agent

[Hint:  $B_2H_6 + 2NaH \longrightarrow 2NaBH_4$  (sodium borohydride). It is used as a reducing agent.]

- Compound Y:
  - (a) has boron in  $sp^2$  hybridized state
  - (b) is a planar molecule

- (c) has zero dipole moment
- (d) is a Lewis base

[Hint: BCl<sub>3</sub>—B in  $sp^2$  state, triangular planar structure and zero dipole moment being symmetrical molecule. It is a Lewis

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#### **THOUGHT 4**

Boron forms a number of hydrides having the general formulae  $B_nH_{n+4}$  and  $B_nH_{n+6}$ . These hydrides are called boranes. The simplest hydride of boron is diborane, B2H6. Boranes contain special types of bonds known as multicentre bonds. Boranes have high heat of combustion.

- 1. The type of hybridization of boron in diborane is:
  - (a) sp
- (b)  $sp^2$
- (c)  $sp^3$
- Three centre two electron bond is present in:
  - (a) BF<sub>3</sub>
- (b)  $B_4H_{10}$
- (c) H<sub>3</sub>BO<sub>3</sub>
- (d)  $B_2H_6$
- 3. Which of the following is electron deficient compound?
  - (a)  $C_2H_6$
- (b) SiH<sub>4</sub>

- (c) PH<sub>3</sub>
- (d)  $B_4H_{10}$
- Which hydride does not exist?
  - (a) BH<sub>3</sub>

- (b)  $H_2F_2$
- (c) SbH<sub>3</sub>

- (d) N<sub>2</sub>H<sub>4</sub>
- 5. From  $B_2H_6$ , all the following can be prepared except:
  - (a)  $H_3BO_3$
- (b)  $B_2(CH_3)_4H_2$
- (c)  $B_2(CH_3)_6$
- (d) NaBH<sub>4</sub>

- $In B_2H_6$ :
  - (a) there is direct boron-boron bond
  - (b) the boron atoms are linked through hydrogen bridges
  - (c) all the B—H bond distances are equal
  - (d) all the atoms are in one plane

,						
Thought 1	<b>1.</b> (b)	<b>2.</b> (c)	<b>3.</b> (d)	<b>4.</b> (d)	<b>5.</b> (a)	<b>6.</b> (d)
Thought 2	1. (a)	<b>2.</b> (b)	<b>3.</b> (c)	<b>4.</b> (b)	<b>5.</b> (d)	
Thought 3	1. (b, c)	<b>2.</b> (c)	3. (a, b)	<b>4.</b> (d)	<b>5.</b> (a,b, c)	
Thought 4	1. (c)	<b>2.</b> (b, d)	3. (d)	<b>4.</b> (a)	<b>5.</b> (c)	<b>6.</b> (b)

## BRAIN STORMING PROBLEMS

- 1. What are special features of structure of boron?
  - [Hint: It is a symmetrical solid with icosahedral shape. There are 20 faces (equilateral triangle). The faces meet at 12 corners. Each icosahedron consist of 12 boron atoms; six of them are bonded to another icosahedron by two centre bond (1.71 Å); each of other six is bonded by a three centre bond (2.02 Å) in separated icosahedra.]
- Which alloy of aluminium is used in air-craft industry? [Ans. Duralumin]
- 3. Aluminium vessels should not be cleaned by washing soda. explain why?

[Ans. Na<sub>2</sub>CO<sub>3</sub> undergo hydrolysis to give NaOH. Sodium hydroxide react with aluminium vessels.

$$2A1 + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$$

4. Can we prepare anhydrous AlCl<sub>3</sub> by heating AlCl<sub>3</sub>·6H<sub>2</sub>O?

[Ans. When AlCl<sub>3</sub>·3H<sub>2</sub>O is heated, hydrolysis takes place.

$$2AlCl_3 \cdot 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl_2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O_1$$

5. When finely powdered aluminium is suddenly exposed to air, it catches fire, explain why?

[Ans. Aluminium powder undergo exothermic oxidation, therefore, it catches fire and becomes hazardous.

$$2Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3$$
;  $\Delta H = -ve (-310 \text{ kJ/mol})$ 

6. Boric acid is weak, it cannot be titrated directly with NaOH. Give the precautions taken in the titration of boric acid with caustic soda.

[Ans. When catechol is added to boric acid, stable compound (strong acid) is formed, which can be titrated with caustic soda using methyl orange indicator.]

7. What do you understand by?

(a) Ammonal

(b) Bentonite

(c) Rubies and Sapphire

(d) Lapis Lazuli

[Hint:

(a) Ammonal: It is mixture of  $\{Al + NH_4NO_3\}$ , used in bombs.

- (b) Bentonite: Alumina-silica clay called 'bentonite' is dropped from aeroplanes in the slury form for spreading water over fires.
- (c) Rubies and sapphire are chemically Al<sub>2</sub>O<sub>3</sub>. These are gems.
- (d) Lapis Lazuli is sodium alumino silicate, which is used as semiprecious stone.]
- **8.** Give the name and structural formula of a boron compound which is optically active.

[Ans. Boro salicylic acid is optically active.]
[Hint:

9. What is the chemical composition of Emery Paper?

[Ans. Impure form of corundum (Al<sub>2</sub>O<sub>3</sub>) containing impurity of Fe<sub>2</sub>O<sub>3</sub> and silica is called Emery and it is used in the manufacture of emery paper or sand paper. This paper is used to polish metals.]

10. Discuss the structure of tricalcium aluminate, which is important constituent of portland cement.

[Hint: General formula = Ca<sub>9</sub>[Al<sub>6</sub>O<sub>18</sub>]. It contains twelve membered rings of Si—O—Si—O bonds made by joining six AlO<sub>4</sub> tetrahedra.]

11. Complete the following reactions:

(i) 
$$BCl_3 + (C_2H_5)_4 \stackrel{+}{N}Cl^- \xrightarrow{CHCl_3}$$
 ?

(ii) 
$$NH_4Cl + Na_2B_4O_7 \xrightarrow{Red hot} ?$$

(iii) 
$$BCl_3 + NH_4Cl \xrightarrow{-140^{\circ}C} ? \xrightarrow{NaBH_4} ?$$

[Ans. (i) 
$$-BCl_3 + (C_2H_5)_4NCl^- \xrightarrow{CHCl_3} [(C_2H_5)_4N]BCl_4$$

(ii) 
$$NH_4Cl + Na_2B_4O_7 \xrightarrow{Red hot} 2BN + B_2O_3 + 2NaCl + 2H_2O_3 + 2H_2O$$

(iii) 
$$3BCl_3 + 3NH_4Cl \xrightarrow{140^{\circ}C} B_3N_3H_3Cl_3$$

 $\xrightarrow{\text{NaBH}_4} \text{B}_3\text{N}_3\text{H}_6 \text{ (Borazine)}]$ 

## INTEGER ANSWER Type Otlestions:

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. How many orbitals of boron are involved in hybridisation in diborane?
- **2.** How many moles of methane are obtained by hydrolysis of one mole of aluminium carbide?
- 3. Colemanite is an important mineral of boron. It is represented  $Ca_2B_xO_{11}\cdot 6H_2O$ . What is the value of x?
- **4.** Borax is represented as Na<sub>2</sub>[B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub>]·8H<sub>2</sub>O. How many tetrahedral boron atoms are present in the structure of borax?
- 5. How many isomers of disubstituted borazine are possible?
- **6.** How much nitrogen is evolved when one gram of ammonium chloride is heated with borax strongly?
- 7. The mass of carbon anode consumed (giving only CO<sub>2</sub>) in the production of 27 kg of aluminium metal from bauxite by electrolytic method is:

## Auswers

- 1. (4) Each boron atom in  $B_2H_6$  is in  $sp^3$ -hybridised state. Thus, four orbitals are involved in hybridisation.
- 2. (3)  $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$ 1 mole 3 moles
- 3. (6)  $Ca_2B_6O_{11}.5H_2O$
- **4.** (2) Borax has two tetrahedral and two triangular units joined together.

$$Na_{2} \begin{bmatrix} OH & & & & & \\ & I & & & & \\ O-B & O-B-O & & & \\ O-B-O & & & & \\ OH & & & OH \end{bmatrix}$$

5. (4) Four isomers are possible. [See Q. No. 15 on page 404]

6. (0) No nitrogen is evolved in this reaction.  $2NH_4Cl + Na_2B_4O_7 \cdot 10H_2O \longrightarrow 2NaCl + 2BN + B_2O_3 + 14H_2O$ 

7. (9) 
$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

Group IVA or 14

Carbon 2s<sup>2</sup>2p<sup>2</sup> Si 32 Ge 4s24p2 Sn 5s25p Pb 114 Jua

# **Elements of Group IVA or 14**

(Elements of Carbon Family,  $ns^2np^2$ )

### 9.1 POSITION IN PERIODIC TABLE

Group IVA or 14 of long form of periodic table consists of six elements—carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb) and ununquadium\*. These six elements constitute a family known as carbon family. These are p-block elements as the last differentiating electron is accommodated in np shell. These elements have four electrons in their valency shell and thus placed in the IVth group. The elements of this group show similarities as well as gradation in properties with rise of atomic number and thus their inclusion in the same group is justified on the basis of electronic configuration and physical and chemical properties which are described below:

Group	ША	IVA	VA	
Period	13	14	15	
2	B (5)	C (6)	N (7)	
3	Al (13)	Si (14)	P (15)	
4	Ga (31)	Ge (32)	As (33)	
5	In (49)	Sn (50)	Sb (51)	
6	T1- (81)	Pb (82)	Bi , (83)	
7	Uut (113)	Uuq (114)	Uup (115)	

### Contents:

- 9.1 Position in Periodic Table
- 9.2 Comparison of Carbon and Silicon
- 9.3. Comparison of Tin and Lead
- Carbon 9.4
- Compounds of Carbon 9.5
- 9.7 Compounds of Silicon
- Tin 9.8
- 9.9 Compounds of Tin
- 9.10 Lead or Plumbum
- 9.11 Compounds of Lead

**1. Electronic configuration :** The electronic configuration of the members of this group are:

Element	At. No.		Electronic configuration	Inert gas core
Carbon	6	2, 4	$1s^2$ , $2s^2$ $2p^2$	[He] $2s^2 2p^2$
Silicon	14	2, 8, 4	$1s^2$ , $2s^2 2p^6$ , $3s^2 3p^2$	[Ne] $3s^2 3p^2$
Germanium	32	2, 8, 18, 4	$1s^2$ , $2s^2 2p^6$ , $3s^2 3p^6 3d^{10}$ , $4s^2 4p^2$	[Ar] $3d^{10}$ , $4s^2 4p^2$
Tin	50	2, 8, 18, 18, 4	$1s^2$ , $2s^2 2p^6$ , $3s^2 3p^6 3d^{10}$ , $4s^2 4p^6 4d^{10}$ , $5s^2 5p^2$	[Kr] $4d^{10}$ , $5s^2$ $5p^2$
Lead	82	2, 8, 18, 32, 18, 4	$1s^2$ , $2s^2 2p^6$ , $3s^2 3p^6 3d^{10}$ , $4s^2 4p^6 4d^{10} 4f^{14}$ , $5s^2 5p^6 5d^{10}$ , $6s^2 6p^2$	[Xe] $4f^{14}$ , $5d^{10}$ , $6s^2 6p^2$
Ununquadium	114	2, 8, 18, 32, 32, 18, 4	$1s^2$ , $2s^2 2p^6$ , $3s^2 3p^6 3d^{10}$ , $4s^2 4p^6 4d^{10} 4f^{14}$ , $5s^2 5p^6 5d^{10} 5f^{14}$ ,	[Rn] $5f^{14}$ , $6d^{10}$ , $7s^2 7p^2$
			$6s^2 6p^6 6d^{10}, 7s^2 7p^2$	

<sup>\*</sup>Recently a new element of this group with atomic number 114 (IUPAC name ununquadium) has been discovered.

The configurations show that these elements have same number of electrons in the valency shell, *i.e.*, 4 electrons in the valency shell, two of which are in s-orbital while remaining two in p-orbitals. Thus, they have  $ns^2 np^2$  configuration, *i.e.*, s-orbital is paired while two p-orbitals are unpaired.

$$\begin{array}{c|c}
ns & np \\
\hline
\uparrow\downarrow & \uparrow & \uparrow
\end{array}$$

The penultimate shell of carbon contains 2 electrons (saturated), of silicon contains 8 electrons (saturated), of germanium contains 18 electrons (saturated) while Sn and Pb contain 18 electrons (unsaturated) each. This shows why carbon differs from silicon in some respects and these two differ from rest of the members of this group. The close resemblance between the elements is quite striking in the case of elements of the first and second groups, but this becomes less evident in the elements of third group and still less evident in the fourth group. It shall be clear from the following discussion.

2. Occurrence of the elements: Carbon is extremely wide spread in nature. It is an essential constituent of all living matter as proteins, carbohydrates and fats. Carbon is the seventeenth and silicon the second most abundant element by mass in the earth's crust. Carbon is found both in native and combined states. Silicon occurs very widely as silica and a wide variety of silicate minerals and clays. Germanium is only found in traces in some silver and zinc ores, and in some types of coal. No doubt that the abundance of tin and lead is comparatively low, but they occur as concentrated ores. Tin is mined as cassiterite, SnO<sub>2</sub> and lead is found as galena ore, PbS. In the fusion reactions occurring on stars and sun, carbon acts as catalyst. The energy released in the process is called stellar energy.

The last member, ununquadium (114) is recently discovered element. It is synthetic, radioactive and unstable element. Not much is known about its properties.

**3. Non-metallic and metallic character:** The change from non-metallic to metallic character with the increase of atomic number is best illustrated by this group. Carbon, the first element, is a non-metal, silicon, the second element has most of the properties of a non-metal but its electrical properties and some of the physical properties are those of a semi-metal (metalloid). Germanium is a metalloid (properties are mixed, *i.e.*, of a metal and a non-metal) while last two members Sn and Pb are distinctly metals.

The change from non-metallic to metallic character is due to less effective nuclear charge and increased number of available orbitals with increase in the size of the atom.

**4. Atomic radii and atomic volume:** Atomic radii and atomic volume increase gradually on moving down the group. The size increases due to the effect of extra shell being added from member to member.

	C	Si	Ge	Sn	Pb
Atomic radius (pm)	77	118	122	140	146
At. volume (mL)	3.4	11.4	13.6	16.3	18.27

It is observed that there is large increase in atomic radius from carbon to silicon but from silicon onwards, the increase is comparatively small from member to member. This is due to the fact that shielding effect of  $s^2p^6$  electrons of the penultimate shell in silicon is large while the shielding effect of  $d^{10}$  electrons in Ge and Sn and  $d^{10}$ ,  $f^{14}$  electrons in Pb is less.

In the same period, the atomic radii of group 14 elements are smaller than the corresponding elements of group 13. This is due to fact that effective nuclear charge increases when we move from group 13 to group 14. This brings contraction in size.

$$C < B$$
 ;  $Si < Al$  ;  $Ge < Ga$  (77 pm) (85 pm) (118 pm) (143 pm) (122 pm) (135 pm)

**5. Ionisation potential:** The ionisation potentials decrease gradually from carbon to lead but not systematically as in groups I and II. The value of lead is slightly higher than expected due to lanthanide contraction.

~		C	Si	Ge	Sn	Pb
Ionisation	$\Delta_i H_1$	1086	786	761	708	715
enthalpy	$\Delta_i H_2$	2352	1577	1537	1411	1450
$(kJ \text{ mol}^{-1})$	$\Delta_i H_3$	4620	3228	3300	2942	3081
	$\Delta_i H_4$	6220	4354	4409	3929	4082

Large decrease in ionisation potential from C to Si is due to increase in size of the atom. Decrease in ionisation potential from silicon onwards is comparatively smaller due to less screening effect of  $d^{10}$  electrons in Ge and Sn and due to  $d^{10}f^{14}$  electrons in Pb.

The slight increase in the ionisation energy from Sn to Pb is due to lanthanide contraction and increase of 32 units of nuclear charge in Pb over Sn, *i.e.* valency electrons are more tightly held in Pb.

The first ionisation energies of group 14 are higher than the corresponding elements of group 13 in the same period.

The increase is due to decrease in size and increase in charge on nucleus of group 14 elements in the same period.

**6. Melting and boiling points:** Carbon has an extremely high melting point (4100°C). Silicon melts appreciably lower than carbon but the values of silicon and germanium are still high. (Si = 1420°C; Ge = 945°C). They have the very stable diamond like structure in which smaller atoms are closely packed. Tin and lead are metallic and have much lower melting points (Sn = 232°C; Pb = 327°C) because the *M*—*M* bonds are weaker. They do not use all the four outer electrons for metallic bonding.

The boiling point of carbon is exceedingly high. It decreases in silicon and then increases in germanium. However, the boiling point decreases from germanium to lead. 7. Electronegativity: The electronegativity values do not decrease in a regular manner. Carbon is the most electronegative element while Si, Ge, Sn and Pb possess nearly the same values. This is due to filling of d-orbitals in Sn and Ge and also f-orbitals in lead.

- **8. Allotropy:** Except lead, all other elements of this group show allotropy. For example, carbon exists as diamond, graphite, coal, charcoal and lampblack; silicon exists in two forms, crystalline and amorphous; germanium exists in two crystalline forms and tin exists in three forms; grey tin, white tin and rhombic tin.
- **9. Valency:** All these elements show a covalency of 4. The tetravalency is explained on the basis of the shifting of one of the paired *ns* electrons to the vacant *np* orbital in the same shell.

Ground state 
$$\begin{array}{c|c}
ns & np \\
\uparrow\downarrow & \uparrow\uparrow \uparrow
\end{array}$$
Excited state 
$$\begin{array}{c|c}
sp^3 \text{ hybridization}
\end{array}$$

These four half filled orbitals mix together to give four  $sp^3$  hybrid orbitals resulting in a tetrahedral structure and each having one unpaired electron.

When  $ns^2$  electrons of outermost shell do not participate in bonding it is called inert pair and the effect is called inert pair effect. The last three elements have a tendency to form  $M^{2+}$  ions as well as  $M^{4+}$  ions. Since, the inert pair effect increases from Ge to Pb, the stability of  $M^{4+}$  ions decreases and that of  $M^{2+}$  ions increases. Thus, the stability of these ions follows the following order:

$$Ge^{2+} < Sn^{2+} < Pb^{2+}$$
  
 $Ge^{4+} > Sn^{4+} > Pb^{4+}$ 

The compounds of Ge<sup>2+</sup> are unstable while compounds of Ge<sup>4+</sup> are stable. Thus, the compounds of Ge<sup>2+</sup> get oxidised into Ge<sup>4+</sup> easily and act as reducing agents.

$$\begin{array}{ccc} Ge^{2+} & \xrightarrow{-2e} & Ge^{4+} \\ \text{Less stable} & \text{More stable} \\ \text{(Reducing agent)} & \end{array}$$

The compounds of  $\mathrm{Sn}^{2+}$  are less stable than  $\mathrm{Sn}^{4+}$ . Thus,  $\mathrm{Sn}^{2+}$  compounds also act as reducing agents. In the case of lead,  $\mathrm{Pb}^{2+}$  compounds are more stable than  $\mathrm{Pb}^{4+}$  compounds. The  $\mathrm{Pb}^{4+}$  compounds, thus, act as oxidising agents.

$$\begin{array}{ccc} \text{Pb}^{4+} & + & 2e \longrightarrow & \text{Pb}^{2+} \\ \text{Less stable} & & \text{More stable} \\ \text{(Oxidising agent)} & & & \end{array}$$

Since  $M^{4+}$  ions are smaller than  $M^{2+}$  ions, in general,  $M^{4+}$  compounds behave as covalent due to high polarisation (small size and high charge) and  $M^{2+}$  compounds are ionic.

10. Multiple bonding: Carbon, the first member of group 14, possesses a pronounced ability to form stable  $p\pi$ – $p\pi$  multiple bonds (double and triple bonds) with itself and with other first row elements such as nitrogen and oxygen. The compounds containing C = C, C = C, C = C, and

C=S bonds are common. Graphite, an allotropic form of carbon, is also an example of  $p\pi-p\pi$  bonding. Silicon and other elements of this group show their reluctance in forming  $p\pi-p\pi$  multiple bonding due to their large atomic sizes. However, silicon and other elements of this group have vacant d-orbitals in their valence shell. These elements can form  $d\pi-p\pi$  double bonds with nitrogen and oxygen. This bond is formed by the donation of an electron pair from filled 2p-orbitals of N or O to the vacant 3d-orbitals of silicon or other elements of group 14. The existence of  $d\pi-p\pi$  bonding explains the structures of trimethylamine, (CH<sub>3</sub>)<sub>3</sub>N, and trisilylamine N(SiH<sub>3</sub>)<sub>3</sub> and their basic nature.

In trimethylamine, the N atom undergoes  $sp^3$ -hybridisation giving tetrahedral configuration. The geometry of the molecule is **pyramidal** as one of the tetrahedral positions is occupied by a lone pair.  $p\pi$ - $d\pi$  bonding cannot occur in this molecule as carbon does not have d-orbitals. This lone pair,  $N(CH_3)_3$ , can be donated to Lewis acids and thus it shows a basic nature. In trisilylamine,  $sp^2$ -hybridisation occurs giving **trigonal planar** geometry to the molecule. The lone pair of electrons is present in unhybridised p-orbital. This overlaps with empty d-orbital of any one of the silicon atoms forming  $p\pi$ - $d\pi$  back bonding. Due to non-availability of lone pair, this molecule does not show basic nature.

**11. Catenation:** The linking of identical atoms with each other to form long chains is called **catenation.** All the elements of this group have the property of catenation. However, this property decreases from carbon to lead. Thus, carbon has the maximum property of catenation, silicon has much lesser tendency, germanium has still lesser tendency whereas tin and lead hardly show this property. The decrease of this property is associated with M—M bond energy which decreases from carbon to lead.

C—C	83 kcal/mol
Si—Si	54 kcal/mol
Ge—Ge	40 kcal/mol
SnSn	37 kcal/mol

The reason for greater tendency of carbon for catenation than other elements may further be explained by the fact that C—C bond energy is approximately of the same value as the energies of bonds between carbon and other elements. On the other hand Si—Si bond is weaker than the bonds between silicon and other elements.

C—C	83 kcal/mol	Si—Si	54 kcal/mol
C—O	86 kcal/mol	Si—O	88 kcal/mol
C—Cl	81 kcal/mol	Si—C	186 kcal/mol

Thus, carbon forms a number of compounds in which a large number of carbon atoms are linked together in the form of straight chains, branched chains or closed rings. The property of catenation is responsible for a very large number of compounds of carbon.

**12. Maximum covalency:** Carbon has only two energy shells, K and L. L shell (outermost shell) has four orbitals 2s,  $2p_x$ ,  $2p_y$  and  $2p_z$ . These four orbitals can accommodate a maximum of 8 electrons forming four covalent bonds. Thus, maximum covalency of carbon is four because it has no d-orbitals or vacant orbitals which can be used to accommodate more electrons.

The remaining elements, however, have vacant *d*-orbitals. These permit the formation of coordinate bonds with other atoms or ions having lone pairs of electrons. For example, SiF<sub>4</sub> can combine with 2F<sup>-</sup> ions.

$$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$$

Thus, the maximum covalency of silicon can be 6. Similarly, other members can show maximum covalency of six involving  $sp^3d^2$  hybridization.

Since all these elements except carbon satisfy the following three conditions for the formation of complexes, they have the tendency to form complexes using *d*-orbitals.

- (i) small size of the atom or ion
- (ii) high charge
- (iii) availability of vacant orbitals of appropriate energy.
- 13. Reactivity: The elements of this group are relatively less reactive but reactivity increases down the group. Lead often appears more unreactive than expected. This is partly due to surface coating of the oxide and partly due to the high overpotential for the reduction of  $H^+$  to  $H_2$  at a lead surface.
- (i) Reactivity towards air: These elements react with the oxygen of the air on strong heating when their oxides are formed.

$$C + O_2 \longrightarrow CO_2$$
;  $Si + O_2 \longrightarrow SiO_2$   
 $Ge + O_2 \longrightarrow GeO_2$ ;  $2Pb + O_2 \longrightarrow 2PbO$ 

Mono-oxides CO, SiO, GeO are also known. SiO is unstable.

(ii) Reactivity towards water: C, Si and Ge are unaffected by water. However, on red heating, these elements except lead decompose steam.

$$C + H_2O \longrightarrow CO + H_2$$
  
 $Si + 2H_2O \longrightarrow SiO_2 + 2H_2$   
 $Sn + 2H_2O \longrightarrow SnO_2 + 2H_2$ 

Lead is unaffected by water, probably, because of a protective oxide film.

(iii) Reactivity towards acids: Non-oxidising acids do not attack carbon and silicon. Germanium is not attacked by dilute HCl. However, when metal is heated in a stream of HCl gas, germanium chloroform is formed.

$$Ge + 3HCl \longrightarrow GeHCl_3 + H_2$$

Tin dissolves slowly in dilute HCl but readily in concentrated HCl.

$$Sn + 2HC1 \longrightarrow SnCl_2 + H_2$$

Lead also dissolves in dilute HCl.

Lead dissolves in concentrated HCl forming chloroplumbous acid, but the reaction stops after sometime due to deposition of PbCl<sub>2</sub>.

$$Pb + 2HCl \longrightarrow PbCl_2 + H_2$$
  
 $PbCl_2 + 2HCl \longrightarrow H_2PbCl_4$ 

Tin dissolves in dilute H<sub>2</sub>SO<sub>4</sub>, conc. H<sub>2</sub>SO<sub>4</sub>, dil. HNO<sub>3</sub> and conc. HNO<sub>3</sub>.

$$Sn + H_2SO_4$$
 (dil.)  $\longrightarrow SnSO_4 + H_2$   
 $Sn + 4H_2SO_4$  (conc.)  $\longrightarrow Sn(SO_4)_2 + 2SO_2 + 4H_2O$   
 $4Sn + 10HNO_3$  (dil.)  $\longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$   
 $Sn + 4HNO_3$  (conc.)  $\longrightarrow H_2SnO_3 + 4NO_2 + H_2O$   
Metastannic  
acid

Lead is not affected by dil. H<sub>2</sub>SO<sub>4</sub>. Hot conc. H<sub>2</sub>SO<sub>4</sub> dissolves lead but the reaction becomes slower due to formation of insoluble PbSO<sub>4</sub>.

$$Pb + 2H_2SO_4 \longrightarrow PbSO_4 + SO_2 + 2H_2O$$

 $HNO_3$  is the best solvent for lead.

$$3Pb + 8HNO_3 (dil.) \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

$$Pb + 4HNO_3 (conc.) \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$$

Organic acids dissolve lead in presence of oxygen.

$$Pb + 2CH_3COOH + 1/2 O_2 \longrightarrow Pb(CH_3COO)_2 + H_2O$$

(iv) Reactivity towards alkalies: Carbon is unaffected by alkalies. Silicon reacts slowly with cold aqueous NaOH and readily with hot solution giving solution of silicate.

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

Sn and Pb are slowly attacked by cold alkali but readily by hot alkali giving stannates and plumbates. Thus, Sn and Pb are somewhat amphoteric.

$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2$$
  
 $Pb + 2NaOH + H_2O \longrightarrow Na_2PbO_3 + 2H_2$ 

#### 14. Compounds:

(i) Hydrides: All the members of this group form covalent hydrides directly or indirectly. The number of hydrides, their stability and the case of formation decreases as we move down from carbon to lead. However, all the members form hydrides of the type  $M \, H_4$ . Besides  $M \, H_4$ , carbon forms a large number of hydrides, saturated as well as unsaturated. Silicon forms only limited number of saturated hydrides. Germanium gives a still smaller number of hydrides while Sn and Pb give only one hydride each.

The hydrides of  $MH_4$  type are gaseous and their thermal stability decreases and consequently the reducing nature increases from top to bottom. However, among the hydrides, silicon hydrides are least stable to hydrolysis.

Hydrides CH<sub>4</sub> SiH<sub>4</sub> GeH<sub>4</sub> SnH<sub>4</sub> PbH<sub>4</sub> Decomposition temp.(°C) 800 450 285 150 0

[The hydrides of silicon (silanes) are much more reactive than the alkanes. The difference in behaviour is attributed to various factors:

(a) Electronegativity values are: C = 2.5, Si = 1.8 and H = 2.1. Thus, the bonding electrons between C and H or Si and H are not equally shared and silicon is vulnerable to attack by nucleophilic reagents.

$$\delta^- \delta^+ \qquad \delta^+ \delta^-$$
  
C—H Si—H

- (b) The larger size of Si is easier to be attacked.
- (c) Si has low energy d-orbitals which may be used to form an intermediate compound and thus lower the activation energy of the process.

$$SiH_4 + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 4H_2$$
  
 $SiH_4 + 3H_2O \longrightarrow H_2SiO_3 + 4H_2$   
 $SiH_4 + 4AgNO_3 \longrightarrow Si + 4Ag + 4HNO_3$   
 $SiH_4 + 2Cl_2 \longrightarrow Si + 4HCl$ 

The low stability of  $GeH_4$ ,  $SnH_4$  and  $PbH_4$  is due to weak M—H bond. It is due to large difference in the size of M and hydrogen atom leading to poor overlapping and weak covalent bond.

[Note: Extremely pure silicon can be obtained by pyrolysis of monosilane, SiH<sub>4</sub>, in absence of air. The pure silicon is used as a semiconductor.

$$SiCl_4 \xrightarrow{LiAlH_4} SiH_4 \xrightarrow{Heat in absence of air} Si(Pure)$$

(ii) Halides: The members of this group form tetrahalides of the type  $MX_4$  except PbBr<sub>4</sub> and PbI<sub>4</sub>. The halides are covalent and formed by  $sp^3$  hybridization. The thermal stability of halides of different elements with a common halogen decreases with increasing atomic number. The thermal stability of tetrahalides of the same element decreases with increase in molecular mass of the tetrahalide.

$$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$$
  
 $CF_4 > CCl_4 > CBr_4 > CI_4$ 

$$\begin{array}{c} Cl & | Cl | H | \\ Cl & | O - H \\ Cl - Si - Cl + 2H_2O \longrightarrow Cl - Si - Cl & \xrightarrow{+H_2O} \\ Cl & | H - O \\ Cl & | H - Cl | \end{array}$$

$$\begin{array}{c|c} OH & OH \\ \hline OH & \hline OH & OH \\ \hline CI-Si-Cl \xrightarrow{+2H_2O} Cl \xrightarrow{+2H_2O} Cl \xrightarrow{+2H_2O} Cl \xrightarrow{+2H_2O} OH \\ \hline OH & OH & OH \\ \hline OH & OH & OH \\ \hline \end{array}$$

[Non-existence of PbBr<sub>4</sub> and PbI<sub>4</sub> can be explained on the basis of strong oxidising nature of Pb<sup>4+</sup>. The ions Br<sup>-</sup> and I<sup>-</sup> are reducing agents, *i.e.*, in presence of these ions, Pb<sup>4+</sup> ions are reduced to Pb<sup>2+</sup> ions.

$$Pb^{4+} + 2Br^{-} \longrightarrow Pb^{2+} + Br_{2}$$
  
 $Pb^{4+} + 2I^{-} \longrightarrow Pb^{2+} + I_{2}$ 

Except carbon halides, other halides are readily hydrolysed by water. The trend towards hydrolysis, however, decreases down the group. The hydrolysis is due to utilisation of d-orbitals to which water molecules can get attached.

The tetrahalides of Si, Ge, Sn and Pb can form hexahalo complexes like  $[SiF_6]^{2-}$ ,  $[GeF_6]^{2-}$ ,  $[GeCl_6]^{2-}$ ,  $[SnCl_6]^{2-}$  and  $[PbCl_6]^{2-}$  with the corresponding halide ions. Thus, tetrahalides of Si, Ge, Sn and Pb act as strong Lewis acids.

Carbon does not form dihalides. All the other elements do form dihalides. There is a steady increase in the stability of dihalides.

$$\operatorname{Si} X_2 < \operatorname{Ge} X_2 < \operatorname{Sn} X_2 < \operatorname{Pb} X_2$$

(iii) Oxides: All the elements of this group form oxides of the type  $MO_2$ .

The acidic nature decreases with increase of atomic number.  $CO_2$  and  $SiO_2$  are acidic while  $GeO_2$ ,  $SnO_2$  and  $PbO_2$  are amphoteric. All these dissolve in alkalies giving carbonates, silicates, germanates, stannates and plumbates, respectively.

$$MO_2 + 2NaOH \longrightarrow Na_2MO_3 + H_2O$$

The dioxides of Ge, Sn and Pb also dissolve in acids.

$$GeO_2 + 4HCl \longrightarrow GeCl_4 + 2H_2O$$
  
 $SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$   
 $PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$ 

They also form oxides of the type MO. SiO is unstable. CO is neutral while SnO and PbO are amphoteric. Basic character of both mono and dioxide increases down the group.

# 9.2 COMPARISON OF CARBON AND SILICON

Carbon and silicon, the first two elements of group 14 have a number of similarities in their properties as both have same number of electrons in the outermost shell. They show many dissimilarities in properties also because the number of electrons in the penultimate shells are different.

#### Points of Similarities

(a) Electronic configuration: Both the elements have 4 electrons, *i.e.*,  $s^2p^2$  grouping in their valence shell.

**(b)** Occurrence: Both are widely distributed in nature. Carbon is the essential constituent of vegetable and animal

kingdom while silicon is an essential constituent of mineral kingdom.

- (c) Non-metallic: Both are typical non-metals. They form oxides of type  $MO_2$  which are acidic in nature. Their monoxides CO and SiO are neutral, SiO is comparatively unstable.
- (d) Valency: Both show tetravalency. Both form covalent compounds by sharing of electrons. Both show tetravalency on account of  $sp^3$  hybridization.
  - (e) Allotropy: Both show allotropy.
- (f) Catenation: Both carbon and silicon possess the property of catenation. Their atoms join with one another in large numbers forming the long chains and rings.
  - (g) Similar compounds:
- (i) Formation of oxides: Both burn in oxygen to form acidic oxides.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$
  
 $SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$ 

(ii) Formation of hydrides: Both form a number of similar hydrides.

## Points of Difference (Dissimilarities)

#### Carbon

1. It has 2 electrons in the penultimate shell.

- 2. It is black solid. It does not melt.
- 3. Some allotropic forms of carbon, e.g., graphite are good conductors of electricity.
- 4. Caustic alkalies have no action on carbon.
- 5. The dioxide, carbon dioxide, is a gas. It has a linear structure. Carbon atom is linked to two oxygen atoms by double covalent bonds. Carbon is sp hybridized. These hybrid orbitals overlap with the porbital of each oxygen atom. The remaining 2p-orbital of each oxygen atom form π-bonds with p-orbitals of carbon atom.

$$O\frac{p-p}{\overline{p-sp}}C\frac{p-p}{\overline{sp-p}}O$$

 ${\rm CO_2}$  molecules are held together by weak van der Waals' forces hence it exists as a gas at ordinary temperatures.

Carbon dioxide dissolves in water and behaves as weak acid.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
Carbonic acid
 $2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$ 

- 6. The lower oxide, carbon monoxide, is known. It is stable and neutral in nature.
- It forms a large number of hydrides known as hydrocarbons which are stable. These are not hydrolysed by water.
- 8. It does not directly react with Cl2 or Br2.
- CCl<sub>4</sub> is a stable compound and it is not hydrolysed by water. The
  hydrolysis does not occur because water molecules cannot be
  coordinated to carbon as its maximum covalency is four.
- The oxyacid, H<sub>2</sub>CO<sub>3</sub>, is unstable. It is best known in the form of salts, carbonates.
- It does not form complex ions as d-orbitals are not present and maximum covalency is four.

$$\begin{array}{cccc} CH_4 & C_2H_6 & C_3H_8 & \cdot C_4H_{10} \\ SiH_4 & Si_2H_6 & Si_3H_8 & Si_4H_{10} \\ (Silane) & (Disilane) & (Trisilane) & (Tetrasilane) \end{array}$$

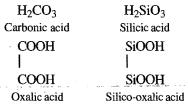
These are all colourless gases and burn in air to form oxides.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
  
 $SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$ 

(iii) Formation of halides: Both form covalent halides of same formula.

CCl <sub>4</sub>	CHCl <sub>3</sub>	$CF_4$
SiCl <sub>4</sub>	SiHCl <sub>3</sub>	SiF <sub>4</sub>

(iv) Formation of acids: Both form similar types of acids.



Silicon

It has 8 electrons in the penultimate shell.

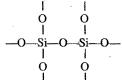
It is reddish brown solid. It melts at 1410°C.

It is bad conductor of heat and electricity.

It reacts with alkalies to evolve hydrogen.

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

The dioxide, silica, is a solid. It has a giant structure. The silicon atom is linked with oxygen atoms by single covalent bonds.



Silica has a three dimensional infinite structure in which silicon is tetrahedrally bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms by covalent bonds. Hence, silica has high melting point and is a solid.

Silica is insoluble in water and acts as a very weak acid.

$$2NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O$$

The SiO is unstable.

It forms lesser number of hydrides which are not very stable. These act as reducing agents. These are hydrolysed by water with evolution of hydrogen.

It reacts with Cl2 or Br2 at 500°C.

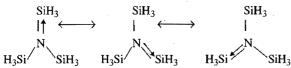
$$Si + 2Cl_2 \xrightarrow{500^{\circ}C} SiCl_4$$

SiCl<sub>4</sub> is less stable and it is hydrolysed by water. The hydrolysis is due to the fact that water molecules can be coordinated to Si as its maximum covalency is six.

The oxyacid,  $H_2SiO_3$ , is stable. It is also known in the form of salts, silicates.

It forms a number of complex ions as d-orbitals are present and maximum covalency is six.

(v) Structure of trimethyl ammonia and trisilyl ammonia: Trimethyl ammonia is pyramidal whereas trisilyl ammonia is a planar molecule. In silicon atom, there is vacant d-orbital hence electron pair of nitrogen is donated to silicon by  $p\pi - d\pi$  overlapping in trisilyl ammonia. Thus, trisilyl ammonia has planar structure.



Trimethyl ammonia has pyramidal shape due to presence of lone pair of electron at nitrogen.

### 9.3 COMPARISON OF TIN AND LEAD

Tin and lead are the last two members of group 14. Both resemble each other in many respects but lead being the last member having higher atomic mass differs in some respects with tin.

#### Points of Similarities

1. Electronic configuration: Both have same electronic configuration having 4 electrons in the outermost shell and 18 electrons in the penultimate shell.

**2. Metallic nature:** Both of them are metals. They have low melting and boiling points.

Element	m.pt. (°C)	b.pt. (°C)
Sn	232	2275
Pb	327	1620

Both are malleable in nature.

- 3. Valency: Both show valency of 4 and 2 in their compounds. It is based on the fact that either 4 or 2 electrons from the outermost shell act as valency electrons. The lower valency, i.e., 2 is shown on account of the inertness of ns pair of electrons. The compounds having divalency are electrovalent while compounds having tetravalency show covalent nature. Both are electropositive metals but also exhibit an electronegative character in some of their compounds. Similar to silicates, the stannates and plumbates are known.
- **4. Action of alkalies:** Both react with hot alkali solutions and liberate hydrogen.

$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2$$
  
 $Pb + 2NaOH + H_2O \longrightarrow Na_2PbO_3 + 2H_2$ 

5. Both form amphoteric oxides of the type MO and  $MO_2$ .

$$SnO + 2NaOH \longrightarrow Na_2SnO_2 + H_2O$$

$$(Sodium stannite)$$

$$SnO + H_2SO_4 \longrightarrow SnSO_4 + H_2O$$

$$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$$

$$(Sodium plumbite)$$

$$PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O$$

**6.** Both form tetrachlorides of the type  $MCl_4$ . These are hydrolysed by water.

$$SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl$$
  
 $PbCl_4 + 2H_2O \longrightarrow PbO_2 + 4HCl$ 

These tetrachlorides combine with HCl to form chloro acids.

H<sub>2</sub>PbCl<sub>6</sub>

Lead

 $Pb + S \longrightarrow PbS$ 

Lead does not show allotropy.

$$\begin{array}{ccc} & & & & & & \\ \text{Chlorostannic acid} & & & & & \\ \text{Tetrachlorides decompose on heating.} & & & & \\ & & & & & \\ \text{SnCl}_4 & \longrightarrow & \text{SnCl}_2 + \text{Cl}_2 \\ \end{array}$$

H<sub>2</sub>SnCl<sub>6</sub>

PbCl<sub>4</sub>  $\longrightarrow$  PbCl<sub>2</sub> + Cl<sub>2</sub>
7. Sulphides of both are precipitated by passing H<sub>2</sub>S through their salt solutions.

$$\begin{array}{c} PbCl_2 \, + \, H_2S \longrightarrow PbS \, + \, 2HCl \\ Black \ ppt. \end{array}$$
 
$$SnCl_2 \, + \, H_2S \longrightarrow SnS \quad + \, 2HCl \\ Yellow \ ppt. \end{array}$$

- 8. Both form tetrahydrides which are unstable.
- 9. Both form organometallic compounds.

Tin

 $Sn + 2S \longrightarrow SnS_2$ 

1. Tin shows allotropy.

 $Sn(C_2H_5)_4$   $Pb(C_2H_5)_4$  Lead tetraethyl

## Points of Difference (Dissimilarities)

rm snows unoutopy.	Lead does not show anodopy.
Tin does not leave any mark	Lead leaves a mark on paper.
* *	
Ductile.	Not very ductile.
Tin is a metalloid.	Lead is a metal.
SnO does not combine with	PbO combines with silica showing
silica.	PbO is more basic than SnO.
	$PbO + SiO_2 \longrightarrow PbSiO_3$
SnCl <sub>2</sub> is soluble in both dil. and	PbCl <sub>2</sub> is insoluble in dil. HCl but
conc. HCl.	soluble in conc. HCl forming
	complex H[PbCl <sub>3</sub> ], H <sub>2</sub> [PbCl <sub>4</sub> ].
SnS is soluble in yellow ammo-	PbS is insoluble in yellow ammo-
nium sulphide showing its acidic	nium sulphide showing its basic
nature.	nature.
Stannic compounds are stable.	Plumbous compounds are stable.
Stannous compounds act as	Plumbic compounds act as oxidis-
reducing agents.	ing agents.
	Lead dissolves in organic acids.
	i -
	retarded by the formation of
	, -
forms metastannic acid with	trate with concentrated nitric acid.
concentrated nitric acid.	•
<del>-</del>	Lead combines with sulphur to
form stannic sulphide.	form lead sulphide.
	Tin does not leave any mark on paper. Ductile. Tin is a metalloid. SnO does not combine with silica.  SnCl <sub>2</sub> is soluble in both dil. and conc. HCl.  SnS is soluble in yellow ammonium sulphide showing its acidic nature.  Stannic compounds are stable. Stannous compounds act as reducing agents. Tin is not attacked by organic acids. The reaction is not retarded with sulphuric acid as sulphates of tin are soluble. Sn forms metastannic acid with concentrated nitric acid. Tin combines with sulphur to

## 9.4 CARBON

## 1. Unique properties of carbon in the group

- 1. Carbon has the smallest atomic radius and lowest atomic volume amongst all the elements of group 14.
- 2. It is most compact. It is the hardest and has highest melting and boiling points amongst the elements of group 14.
- 3. It has the highest ionisation energy and is most electronegative element of group 14.
- 4. Its maximum covalency is 4 as d electrons are absent in the valency shell.
- 5. It has maximum property of catenation. It can form multiple bonds. As a result, carbon forms a large number of compounds.
- 6. Carbon dioxide, CO<sub>2</sub>, is a gas while the dioxides of other elements are solids.
- 7.  $CCl_4$  does not undergo hydrolysis while the tetrahalides,  $MX_4$ , of other elements undergo hydrolysis.

#### 2. Occurrence

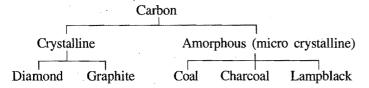
Carbon is one of the most widely distributed elements in nature. It occurs free as well as in the combined state. It occurs free in crystalline form as diamond, graphite, and in the amorphous form as coal. It is present in all living organisms, plants and animals, in the combined state in the form of proteins, carbohydrates, fats and other complicated compounds. It is present as hydrocarbons in natural gas and petroleum. It occurs as carbon dioxide and carbon monoxide in atmosphere. In mineral world, it occurs in the form of carbonates such as limestone, CaCO<sub>3</sub>; magnesite, MgCO<sub>3</sub>; calamine, ZnCO<sub>3</sub>; dolomite, MgCO<sub>3</sub>·CaCO<sub>3</sub>; siderite, FeCO<sub>3</sub>; cerussite, PbCO<sub>3</sub>; etc.

## 3. Allotropic forms of carbon

The property due to which an element exists in two or more forms which differ in their physical and some of the chemical properties is known as allotropy and the various forms are called allotropes or allotropic modifications. This phenomenon is due to the difference either in the number of atoms in the molecules [as in the case of oxygen (O<sub>2</sub>) and ozone (O<sub>3</sub>)] or arrangement of atoms in the molecules (as in the case of various forms of carbon).

Carbon exists in two allotropic forms:

(a) Crystalline and (b) amorphous. The crystalline forms are diamond and graphite while the amorphous forms are coal, charcoal, lampblack, etc.



- (a) Diamond: (i) It is the purest form of carbon.
- (ii) It is found naturally as well as obtained artificially.
- (iii) It is the hardest natural substance known.
- (iv) It is transparent and has a specific gravity 3.52.
- (v) It is a bad conductor of heat and electricity. It is transparent to X-rays and glows in ultraviolet rays with bluish green colour.
- (vi) Its refractive index is high (2.45) and when properly cut, it produces maximum total internal reflection which is responsible for its brilliance.
- (vii) It is chemically inert. It is not attacked by acids, alkalies and salts. It burns in air on heating at  $900^{\circ}$ C to form  $CO_2$ . It reacts with fluorine at  $700^{\circ}$ C to form  $CF_4$ .

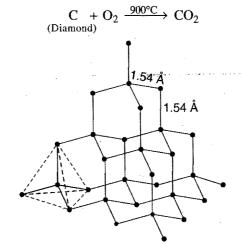


Fig. 9.1 Structure of diamond

$$C + 2F_2 \xrightarrow{700^{\circ}C} CF_4$$

The important properties of diamond are related to its structure. In diamond, each carbon atom is in  $sp^3$  hybridized state and linked to four other carbon atoms tetrahedrally by covalent bonds. This gives a giant three dimensional polymeric structure in which C—C distance is 1.54 Å and bond angle is  $109.5^{\circ}$ .

As the atoms are held firmly by strong covalent bonds, diamond is the **hardest substance**, possesses very high melting point (3600°C) and chemically inert. Since there is no mobile electron present, diamond is non-conductor of electricity.

Uses: Diamond is used as a gem stone on account of reflection and refraction of light. Impure diamonds (black) are used in knives for cutting glass, "Diamond studded saws" in drill bits, as rock borers and is also used as polishers.

**(b) Graphite:** (i) It is found in nature and also manufactured by Acheson process. Anthracite is heated with sand in an electric furnace of the resistance type. It is fitted with two carbon electrodes joined by a thin carbon rod through which an alternating current is passed (Fig. 9.2).

The charge is heated at 3000°C for 24–30 hours. Silicon carbide is formed first which decomposes at high temperature into graphite and silicon. Silicon volatilizes away leaving behind graphite.

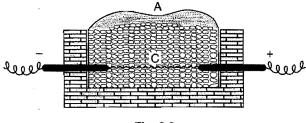


Fig. 9.2

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

$$\downarrow \qquad \qquad C + Si$$
(Graphite)

- (ii) It is a soft, greasy, dark greyish coloured crystalline solid.
  - (iii) Its density is 2.5 g mL<sup>-1</sup>.
- (iv) It is good conductor of electricity and its conductivity increases with temperature.
- (v) It leaves a black mark on paper and is called **black lead** or **plumbago.**
- (vi) It is chemically more active than diamond. It ignites in air or oxygen at  $700^{\circ}$ C to form  $CO_2$ . It is not attacked by alkalies and dilute acids. However, when treated with concentrated HNO<sub>3</sub> or concentrated H<sub>2</sub>SO<sub>4</sub>, it is oxidised to insoluble yellowish green substance known as graphitic acid,  $C_{11}H_4O_5$ . With alkaline potassium permanganate, it is oxidised to mellitic acid  $[C_6(COOH)_6]$  and oxalic acid. It forms  $CO_2$  with chromic acid.

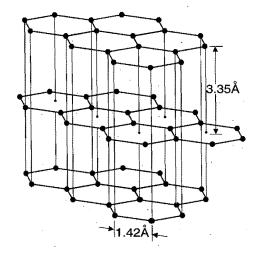


Fig. 9.3 Structure of graphite

It has a two dimensional sheet structure. Each carbon atom is in  $sp^2$  hybridized state and is linked to three other carbon atoms in a hexagonal planar structure. As there are four valence electrons in each carbon atom, after forming three C—C bonds, each carbon atom is left with one spare electron in its p-orbital. This electron then overlaps with each other to form a  $\pi$ -bond. Hence, the C—C distance in graphite is shorter (1.42 Å) than that of diamond (1.54 Å). The  $\pi$ -electrons are

free to move throughout the entire layers, graphite is good conductor of electricity. The adjacent layers are held by weak van der Waals' forces and the distance between two layers is sufficiently large (3.4 Å). Thus, two adjacent layers can easily slide over each other and hence graphite is soft and possesses low density. The more reactivity of graphite is due to the presence of mobile electrons. Graphite is of two forms:  $\alpha$  and  $\beta$ .

In  $\alpha$ -graphite layers are arranged in sequence ABAB, with the third layer exactly above first layer. In  $\beta$ -graphite, the layers are arranged as ABCABC........ The two forms are interconvertible.

Graphite is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less than diamond.

Graphite 
$$\frac{1600^{\circ}\text{C}}{50000-60000 \text{ atm.}}$$
 Diamond

When graphite is heated with vapours of K, Rb, Cs at  $300^{\circ}$ C, it forms  $C_8M$ . Graphite is diamagnetic but  $C_8M$  is paramagnetic.

**Uses:** Graphite is used:

- (i) for lining and making electrodes of electric furnaces.
- (ii) in making refractory crucibles.
- (iii) in making lead pencils.
- (iv) as a moderator in nuclear reactor.
- (v) as a lubricant in machinery.
- (c) Coal: It is the crude form of carbon. It has been formed in nature as a result of slow decomposition of vegetable matter under the influence of heat, pressure and limited supply of air. It is found in various forms which represent the different stages of transformation of vegetable matter. The successive stages of transformation are: peat, lignite, bituminous, steam coal and anthracite. The carbon contents of these forms along with calorific values are given below:

	Peat	Lignite	Bituminous	Steam coal	Anthracite
Carbon content %.	60	67	88	93	95
Calorific value	.9900	11,700	14,950	15,720	16,200
(B.Th.U. per 1b)			· ·		

[1 B.Th.U. = 252 calories or 397 B.Th.U. = 1 kcal.]

The common variety of coal is bituminous. It is hard like stone and burns with smoky flame. The superior quality is anthracite which burns with non-smoky flame.

When coal is subjected to destructive distillation by heating in the absence of air, it loses volatile constituents such as coal gas, ammonia, benzene, phenol and tar, the residue left behind is coke. Thus, coke is an artificial product. It is coal minus volatile matter.

**Uses:** Coal is mainly used: (i) as a fuel. (ii) for the manufacture of coal gas, coal tar and coke. (iii) in the manufacture of synthetic petrol.

Coke is used: (i) as a reducing agent in iron and steel industry. (ii) as a fuel. (It burns without smoke) (iii) for making fuel gases and graphite.

(d) Charcoal: This form of carbon is obtained by burning wood, cellulose or any other carbonous matter in a limited supply of air. Charcoal is of various forms such as wood charcoal, sugar charcoal, coconut charcoal, animal charcoal, etc. These forms contain varying amounts of carbon content. A very pure form of carbon is obtained from sugar. Wood charcoal is porous and has a very large surface area per unit weight. It is, therefore, used as an adsorbent. When charcoal is given a special treatment in order to increase its absorption capacity, the resulting material is known as activated charcoal and the process of treatment is called activation. Activation is carried out by heating the charcoal in retorts at 800-850°C in a current of superheated steam. This removes the impurities sticking on the surface and blocking the capillary pores.

Charcoal is the most active form of carbon. It easily burns in air to form  $CO_2$ . It reacts with many oxidising agents. It is affected by conc.  $HNO_3$  and conc.  $H_2SO_4$ .

$$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$$
  
 $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$ 

Uses: Charcoal is used:

- (i) in removing offensive odour from air in the airconditioning processes.
- (ii) in making filters in cigarettes as to remove vapours of nicotine.
  - (iii) in removing fused oil from crude spirit.
- (iv) in decolourising sugar syrup and refining oils, fats, glycerine, etc.
- (v) in treatment of drinking water after chlorination as it adsorbs excess of chlorine.
  - (vi) in gas masks as it adsorbs poisonous gases.
- **(e)** Lampblack or carbon black or soot: It is obtained by burning substances rich in carbon content such as kerosene, petroleum, turpentine oil, acetylene, etc., in a limited supply of air. These substances yield a large amount of smoke which is passed into chambers having wet blankets. The soot collected on these blankets is called lampblack.

It is almost pure carbon. The carbon content is as high as 98–99% with a small impurity of hydrocarbon. Lampblack is a soft black powder. It is used for making printing inks, black paints, Indian ink, boot polishes and ribbons of typewriters. The main application, at present, is as a filler in making rubber tyres.

## **4. Fullerenes or Bucky balls**

Chemistry is full of surprises and the discovery of a new series of allotropes of carbon must rank as one of the most unexpected findings of all.

Fullerenes constitute a family of structures in which carbon atoms are arranged in a spherical or elliptical structure. To make such a structure, the carbon atoms form five or six-membered rings, similar to the pattern of lines on a soccer ball. One of the most interesting carbon molecules, made in 1985, as a result of action of a laser beam on a sample of graphite

is  $C_{60}$ . It was given the name of **buckminster fullerene**. It is made from interlocking hexagonal and pentagonal rings of carbon atoms. The  $C_{60}$  molecule structure is shown in Fig. 9.4. Such molecules are now thought to exist even in chimney soot or candle soot. Each carbon is  $sp^2$  hybridised. The average  $\dot{C}$ —C distance is 144 pm.

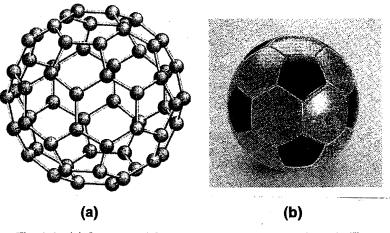


Fig. 9.4 (a) Structure of C<sub>60</sub>, buckminsterfullerene a "buckyball"
 (b) The buckminsterfullerene molecule is often called "buckyball" because of its football appearance

Another molecule  $C_{70}$  has been recently discovered. These and similar large carbon molecules are sometimes referred as **bucky balls.** This allotrope family was named after R. Buckminster Fuller, a genius architect of the twentieth century.

One method of manufacturing the fullerenes is to use an intense laser beam to heat graphite to temperatures of over 10,000°C. At these temperatures, sections of the hexagonal planes of carbon atoms peel off the surface and wrap themselves into balls.

Diamond and graphite are insoluble in all solvents but fullerenes are highly soluble in nonpolar solvents such as hexane and toluene. Although black in solid phase, fullerenes display a wide range of colours in solution. All the fullerenes sublime when heated. The  $C_{60}$  molecules pack together in the same way as metal atoms do, forming a face centred cubic arrangement. The fullerenes have low densities (about 1.5 g cm<sup>-3</sup>) and they are non-conductors of electricity. All the carbon atoms in buckminster fullerene are  $sp^2$  hybridized because all carbon atoms are equivalent, the strain caused by distortion of the bonds from coplanarity is equally distributed among all the carbon atoms. Thus, this molecule is quite stable.

The fullerenes are easily reduced to anions by reaction with alkali and alkaline earth metals. For example, rubidium fits within the interstices in the  $C_{60}$  lattice to give  $Rb_3C_{60}$ . This compound is a super conductor at temperatures below 28K. Chemical reaction with the surface of the fullerenes is also possible; thus reaction with fluorine results in the formation of  $C_{60}F_{60}$ .

Besides  $C_{60}$  and  $C_{70}$ , even-numbered fullerenes from  $C_{70}$  to  $C_{100}$  are known. Only recently, a fullerene  $C_{36}$  has been established. It is a black solid and gives a golden-yellow solution.

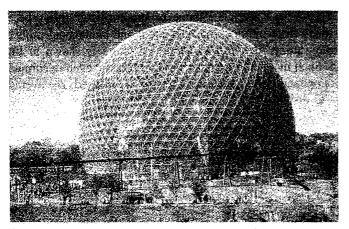


Fig. 9.5 The American Pavilion at the Montréal Expo in 1967 was geodesic dome designed by R. Buckminster Fuller. The dome is a three-quarter sphere, 200 feet high and 250 feet in diameter.

## 5. Chemical properties of carbon

Charcoal has the enormous surface area and hence, it is the most reactive form of carbon. The other forms such as diamond, graphite, coal, etc., which are denser, are less reactive in nature.

(a) Combustion: All the allotropic forms of carbon burn in air or oxygen forming carbon dioxide (when oxygen supply is sufficient) and carbon monoxide (when oxygen supply is insufficient).

$$C + O_2 \longrightarrow CO_2$$
 (Carbon dioxide)  
 $2C + O_2 \longrightarrow 2CO$  (Carbon monoxide)

This property shows that all the allotropic forms are chemically identical.

**(b) Reducing agent:** Carbon is a strong reducing agent. It reduces many metallic oxides to corresponding metals, sulphates into sulphides and water to hydrogen. These reactions occur at high temperatures.

$$ZnO + C \longrightarrow Zn + CO$$
 $PbO + C \longrightarrow Pb + CO$ 
 $PbSO_4 + 4C \longrightarrow PbS + 4CO$ 
 $BaSO_4 + 4C \longrightarrow BaS + 4CO$ 
 $C + H_2O \xrightarrow{Red hot} CO + H_2$ 

(c) Combination with other elements: It combines with sulphur when the vapours of sulphur are passed over red hot carbon forming carbon disulphide.

$$C + 2S \longrightarrow CS_2$$

When electric arc is struck between carbon electrodes in presence of hydrogen, acetylene is formed.

$$2C + H_2 \longrightarrow C_2H_2$$

Beryllium when heated with carbon forms carbide

$$2\text{Be} + \text{C} \longrightarrow \text{Be}_2\text{C}$$

Various carbides are formed when carbon is heated with certain oxides.

$$CaO + 3C \xrightarrow{2000^{\circ}C} CaC_2 + CO$$

$$Calcium \ carbide$$

$$SiO_2 + 3C \xrightarrow{2000^{\circ}C} SiC + 2CO$$

$$Silica \qquad Carborundum$$

$$2Al_2O_3 + 9C \xrightarrow{2000^{\circ}C} Al_4C_3 + 6CO$$

(d) Reactivity towards acids: Charcoal dissolves slowly in hot dilute HNO<sub>3</sub> forming a brown coloured substance, artificial tannin. Conc. HNO<sub>3</sub> oxidises carbon to carbon dioxide.

$$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$$

Hot and conc. H<sub>2</sub>SO<sub>4</sub> also oxidises it to carbon dioxide. A small quantity of mellitic acid (benzene hexacarboxylic acid) is also formed.

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$
  
 $12C + 9H_2SO_4 \longrightarrow C_6(COOH)_6 + 6H_2O + 9SO_2$ 

## 9.5 COMPOUNDS OF CARBON

#### 1. Oxides of Carbon

Two oxides of carbon, carbon monoxide and carbon dioxide are important and described below:

## (a) Carbon Monoxide, CO

It is found in small amounts in volcanic gases, chimney gases, exhaust gases of internal combustion engines and coal gas.

**Preparation:** The following methods can be applied for the preparation of carbon monoxide:

(i) By heating oxalic acid with concentrated sulphuric acid: A mixture of CO and CO<sub>2</sub> is obtained. Sulphuric acid acts as a dehydrating agent. CO<sub>2</sub> is removed by passing the gaseous mixture through caustic soda or caustic potash solution.

$$\begin{array}{c|c} \text{COOH} & \xrightarrow{\text{H}_2\text{SO}_4} & \text{CO} + \text{CO}_2 \\ \hline \text{COOH} & \xrightarrow{\text{-H}_2\text{O}} & \text{CO} + \text{CO}_2 \end{array}$$

Similarly by heating formic acid with concentrated H<sub>2</sub>SO<sub>4</sub>, only CO is obtained.

$$\text{HCOOH} \xrightarrow{\text{H}_2\text{SO}_4} \text{CO}$$

(ii) By the reduction of oxides of heavy metals with carbon: On heating oxides of heavy metals with carbon, CO is formed.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
  
 $ZnO + C \longrightarrow Zn + CO$ 

(iii) By reduction of carbon dioxide:  $CO_2$  can be reduced with carbon or zinc at high temperatures.  $CO_2$  when passed over red hot zinc, a mixture of CO and  $CO_2$  is obtained.

$$Zn + CO_2 \xrightarrow{Heat} ZnO + CO$$

Similarly, when  $CO_2$  is passed over red hot charcoal, the reduction of  $CO_2$  into CO occurs with the formation of a mixture of  $CO_2$  and CO. The gaseous mixture is passed through NaOH or KOH solution as to remove  $CO_2$ .

(iv) By heating carbonates of calcium, barium or magnesium with zinc, CO is obtained.

$$MgCO_3 + Zn \longrightarrow MgO + ZnO + CO$$

(v) By heating potassium ferrocyanide with conc.  $H_2SO_4$ : When potassium ferrocyanide in powdered state is heated with concentrated  $H_2SO_4$ , CO is evolved. Dilute  $H_2SO_4$  should never be used because it shall evolve highly poisonous gas, HCN.

$$K_4Fe(CN)_6 + 3H_2SO_4 \longrightarrow 2K_2SO_4 + FeSO_4 + 6HCN$$
  
 $6HCN + 12H_2O \longrightarrow 6HCOOH + 6NH_3$   
 $Formic acid$   
 $6NH_3 + 3H_2SO_4 \longrightarrow 3(NH_4)_2SO_4$   
 $6HCOOH \xrightarrow{H_2SO_4} 6CO + 6H_2O$ 

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 6CO + 3(NH_4)_2SO_4$$

**Manufacture:** Carbon monoxide is obtained in the form of water gas and producer gas when air (moist) is passed over a bed of white hot coke. The following reactions may occur.

$$2C + O_2 \longrightarrow 2CO$$

$$C + O_2 \longrightarrow CO_2$$

$$C + H_2O \longrightarrow \underbrace{CO + H_2}_{Water gas}$$

Carbon dioxide is reduced by passing the mixture over heated charcoal.

$$CO_2 + C \longrightarrow 2CO$$

The CO produced, always consists of  $N_2$ ,  $H_2$ ,  $CO_2$ , etc. **Properties:** (i) It is a colourless and odourless gas.

- (ii) It is slightly soluble in water.
- (iii) It is a combustible gas but does not support combustion.
- (iv) Its density is nearly equal to the density of air.
- (v) It is highly poisonous in nature. One part in 100 parts of air causes death in few minutes. The poisonous nature of CO is due to the fact that it combines with haemoglobin (a red colouring matter of blood which is absorber of oxygen) to form **carboxy-haemoglobin** which is not a able to absorb oxygen and as a result of this, suffocation and as place. This phenomenon is known as ASPHYXIA.
  - (vi) It is not decomposed by heat.

- (vii) It is neutral to litmus.
- (viii) It burns with blue flame to form CO<sub>2</sub>. This is an exothermic process.

$$2CO + O_2 \longrightarrow 2CO_2 + Heat$$

(ix) It is a good reducing agent as it takes up oxygen and converted into CO<sub>2</sub>. This property is utilised for the extraction of metals from their oxides.

$$Fe_2O_3 + 3CO \xrightarrow{600-900^{\circ}C} 2Fe + 3CO_2$$

$$ZnO + CO \longrightarrow Zn + CO_2$$

$$PbO + CO \longrightarrow Pb + CO_2$$

It reduces Fehling's solution also.

$$2Cu(OH)_2 + CO \longrightarrow Cu_2O + 2H_2O + CO_2$$

It reduces  $I_2O_5$  into iodine.

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

(x) The bonding in carbon monoxide is represented as,

Thus, all the four valencies of carbon are not satisfied. It behaves as unsaturated compound and forms addition products with a number of substances.

$$\begin{array}{c} \text{CO} + 2\text{H}_2 \xrightarrow{\hspace{0.2cm} 150-400^{\circ}\text{C}} & \text{CH}_3\text{OH} \\ \text{Methyl alcohol} \\ \text{CO} + \text{Cl}_2 \xrightarrow{\hspace{0.2cm} \text{Sunlight} \\ \text{or camphor}} & \text{COCl}_2 \\ \text{Phosgene} \\ \\ \text{CO} + \text{S} \xrightarrow{\hspace{0.2cm} \text{Heat}} & \text{COS} \\ \text{Carbonyl sulphide} \\ \text{CO} + \text{NaOH} \xrightarrow{\hspace{0.2cm} \text{Under} \\ \text{pressure}} & \text{HCOONa} \\ \text{Sodium formate} \\ \\ \text{CuCl} + \text{CO} \xrightarrow{\hspace{0.2cm} \text{High} \\ \text{pressure}} & \text{CuCl} \cdot \text{CO} \\ \text{Addition} \\ \text{soln.)} & \text{product} \\ \end{array}$$

It combines with metals like Cr, Ni, Fe, etc. The compounds thus formed are called carbonyls.

Ni + 4CO 
$$\xrightarrow{80^{\circ}\text{C}}$$
 Ni(CO)<sub>4</sub>  
Fe + 5CO  $\xrightarrow{180^{\circ}\text{C}}$  Fe(CO)<sub>5</sub>

These reactions are used in the extraction and purification of metals.

**Uses:** (i) It is used as a fuel in the form of water gas  $(CO + H_2)$  and producer gas  $(CO + N_2)$ .

- (ii) CO is used in the manufacture of methanol, synthetic petrol, formic acid and phosgene gas (highly poisonous gas).
  - (iii) It is used as a reducing agent in the extraction of iron.
  - (iv) It is used in the extraction of nickel (Mond's process).

**Structure:** The electronic structure of carbon monoxide may be represented as follows:

$$:\bar{c}:::\bar{o}: \text{ or } :\bar{c}=\bar{o}: \text{ or } :c \subseteq o$$

Carbon atom is sp hybridized. One sp-orbital is being used to form a single bond with oxygen atom while the other sp-orbital which points away from the C—O bond contains a lone pair of electrons. The remaining two unhybridized p-orbitals form two  $\pi$ -bonds with two p-orbitals of oxygen atoms. The presence of a triple bond is evidenced by the following facts:

- (i) The bond length between carbon and oxygen is 1.13 Å which corresponds to carbon-oxygen triple bond.
  - (ii) The value of dipole moment is small.
- (iii) Due to presence of lone pair of electrons on carbon, carbon monoxide molecule acts as a ligand and can form a coordinate bond with certain metals  $(M \leftarrow C \stackrel{\leftarrow}{=} O)$ .

## (b) Carbon Dioxide, CO<sub>2</sub>

**Occurrence:** It is present in atmosphere to the extent of 0.03–0.05 per cent. It comes to the atmosphere from animal breathing, decay of vegetable matter, burning of carbon and carbonous matter, etc. It is also utilised by plants in photosynthesis. Thus, a carbon dioxide cycle is operating in nature and the proportion of  $CO_2$  in the atmosphere remains about the same. It is found in combined state in the form of carbonates.

**Preparation:** The following methods are used for its preparation:

(i) By the complete combustion of carbon: Carbon is burnt in free supply of air.

$$C + O_2 \longrightarrow CO_2$$

If CO is formed, it also burns with pale blue flame forming carbon dioxide.

$$2C + O_2 \longrightarrow 2CO$$
$$2CO + O_2 \longrightarrow 2CO_2$$

(ii) By the action of dil. mineral acids on carbonates and bicarbonates: Mineral acids react with carbonates and bicarbonates and evolve carbon dioxide.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$
  
 $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$   
 $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$ 

This method is used in the laboratory for the formation of carbon dioxide. Marble pieces ( $CaCO_3$ ) are taken in Woulfebottle which is fitted with a thistle funnel and a delivery tube. The other end of the delivery tube is kept into a dry cylinder through a card board disc. Pieces of marble are first covered with water and then concentrated HCl is added through the funnel.  $CO_2$  is formed which is collected by upward displacement of air.

Sulphuric acid is not used for the preparation because calcium sulphate formed gets deposited on the pieces of marble. This prevents the further action of  $H_2SO_4$  on marble pieces.

(iii) By heating carbonates and bicarbonates: The carbonates of less electropositive metals on heating decompose evolving carbon dioxide.

$$ZnCO_3 \longrightarrow ZnO + CO_2$$
  
 $CuCO_3 \longrightarrow CuO + CO_2$ 

Bicarbonates of all the metals decompose on heating with evolution of CO<sub>2</sub>.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$
  
 $Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$ 

**Manufacture:** (i) From fuel gases: The fuel gases produced during the combustion of coal or coke contain large amounts of carbon dioxide mixed with nitrogen, carbon monoxide, oxygen, etc. These gases are passed through  $K_2CO_3$  solution which absorbs  $CO_2$ .

$$K_2CO_3 + CO_2 + H_2O \longrightarrow 2KHCO_3$$

This solution is then boiled when CO<sub>2</sub> is liberated.

$$2KHCO_3 \longrightarrow K_2CO_3 + H_2O + CO_2$$

(ii) From lime kilns: When lime is manufactured by the calcination of lime stone, (CaCO<sub>3</sub>), carbon dioxide is obtained as a by-product.

$$CaCO_3 \longrightarrow CaO + CO_2$$

(iii) From fermentation: During fermentation; when molasses are changed into alcohol, a large amount of CO<sub>2</sub> is obtained as a by-product.

$$\underset{Glucose}{Sugar} \longrightarrow \underset{Glucose}{C_6H_{12}O_6} \longrightarrow 2C_2H_5OH + 2CO_2$$

**Properties:** (i) It is a colourless, odourless and tasteless gas.

- (ii) It is slightly soluble in water under ordinary pressure but at high pressures, the solubility is high.
  - (iii) It is heavier than air.
- (iv) It is easily liquefied under pressure into a colourless mobile liquid. If CO<sub>2</sub> under pressure is allowed to escape through a nozzle, a white solid, *i.e.*, **dry ice** is obtained. Solid CO<sub>2</sub> is a soft, white, snow like substance. It sublimes and leaves no residue. Solid CO<sub>2</sub> is used as a refrigerant under the commercial name **drikold**. It is used in the transport of perishable food materials. It provides cold as well as the inert atmosphere which helps in killing the undesirable bacteria.
- (v) It is neither combustible nor a supporter of combustion. However, burning magnesium, sodium or potassium continues burning in the gas.

$$CO_2 + 2Mg \longrightarrow 2MgO + C$$

$$CO_2 + 4Na \longrightarrow 2Na_2O + C$$

$$\downarrow^{CO_2}$$

$$Na_2CO_3$$

[Note: CO<sub>2</sub> is used as fire extinguisher but it cannot be used in the case of active metal fires which have affinity for oxygen.]

(vi) CO<sub>2</sub> acts as an oxidising agent. When heated with Zn, iron or carbon, these are oxidised.

$$Zn + CO_2 \longrightarrow ZnO + CO$$
  
 $CO_2 + C \longrightarrow 2CO$ 

(vii) CO<sub>2</sub> is an acidic oxide. It dissolves in water forming unstable carbonic acid.

$$H_2O + CO_2 \Longrightarrow H_2CO_3$$

It combines with alkalies to form two series of salts, carbonates and bicarbonates.

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

With excess of CO<sub>2</sub>, carbonate is converted into bicarbonate.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

Lime water, Ca(OH)<sub>2</sub>, is turned milky on passing CO<sub>2</sub> with the formation of insoluble calcium carbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
Insoluble

The milkiness disappears on passing more of CO<sub>2</sub> with the conversion of calcium carbonate into soluble calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$
Soluble

(viii) CO<sub>2</sub> reacts with basic oxides like Na<sub>2</sub>O, K<sub>2</sub>O, etc.,to form corresponding carbonates.

$$K_2O + CO_2 \longrightarrow K_2CO_3$$
  
 $Na_2O + CO_2 \longrightarrow Na_2CO_3$ 

(ix) CO<sub>2</sub> is converted by plants in the presence of sunlight and chlorophyll into glucose and higher carbohydrates. This process is known as photosynthesis.

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

Uses: (i) It is used in the manufacture of aerated water.

- (ii) Solid  $\rm CO_2$  (dry ice) is used in refrigeration. It is superior refrigerant than common ice because it can produce very low temperatures and does not form liquid on melting. A mixture of solid  $\rm CO_2$  and ether is used to produce low temperature of the order of  $-80^{\circ}\rm C$  to  $-100^{\circ}\rm C$ .
- (iii) Carbogen is a mixture of  $O_2$  and  $CO_2$  (5–10%). It is used for artificial respiration in the case of pneumonia patients and victims of CO poisoning.
- (iv) It is used in the manufacture of white lead and sodium carbonate (Solvay process).
- (v) CO<sub>2</sub> is used as fire extinguisher. The use of common fire extinguisher is based on the production of CO<sub>2</sub>. A soda acid fire extinguisher contains a concentrated solution of sodium bicarbonate and a bottle containing concentrated sulphuric acid. When the apparatus is turned upside down the acid flows out of the bottle and reacts with sodium bicarbonate to produce CO<sub>2</sub>.

Aluminium sulphate in place of conc. $H_2SO_4$  is used in foam type fire extinguishers. When solution of NaHCO<sub>3</sub> and aluminium sulphate react,  $CO_2$  is liberated along with the hydrolysis of aluminium sulphate producing aluminium hydroxide in the form of foam.

$$Al_2(SO_4)_3 + 6NaHCO_3 \longrightarrow 2Al(OH)_3 + 3Na_2SO_4 + 6CO_2$$
  
 $Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4$ 

Al(OH)<sub>3</sub> deposits on the burning articles and thus cuts off their contact with the air.

(vi) CO<sub>2</sub> is used by plants in the form of food.

**Structure:** CO<sub>2</sub> has a linear structure since its dipole moment is zero. Both the oxygen atoms are linked by double bonds.

$$O = C = O$$

The C—O bond length is 1.15 Å which is less than calculated value of double bond C—O. Thus, it is believed that CO<sub>2</sub> molecule is a resonance hybrid of the following structures:

$$0=C=0 \longleftrightarrow \overset{+}{0}=C-\overset{-}{0} \longleftrightarrow \overset{-}{0}-C=\overset{+}{0}$$

The formation of the molecule can be explained on the basis of hybridization. Carbon is sp- hybridized. The hybrid orbitals form sigma bonds with p-orbitals of each oxygen atoms. The unhybridized two p-orbitals of carbon atom form two  $\pi$ -bonds with two oxygen atoms.

Carbon forms some less stable oxides, e.g.,  $C_3O_2$ ,  $C_5O_2$  and  $C_1O_2O_3$ . Graphite oxides are  $C_2O_3$  and  $C_2O_3$  which are still less stable. Carbon suboxide is formed by dehydration of malonic acid.

$$CH_2 \stackrel{COOH}{\underbrace{\qquad \qquad \qquad \qquad \qquad \qquad }} O=C=C=C=O+2H_2O$$

Some important reactions of carbon suboxide are:

$$C_{3}O_{2} + 2H_{2}O \longrightarrow CH_{2}$$

$$COOH$$

$$Malonic acid$$

$$COCI$$

$$C_{3}O_{2} + 2HCI \longrightarrow CH_{2}$$

$$COCI$$

$$Malonyl chloride$$

$$C_{3}O_{2} + 2NH_{3} \longrightarrow CH_{2}$$

$$CONH_{2}$$

$$CONH_{2}$$

$$Malonyl amide$$

# 2. Carbonic Acid, Carbonates and Bicarbonates

Carbon dioxide is an acidic oxide. The solution of CO<sub>2</sub> in water shows feeble acidic nature. This is believed due to the formation of carbonic acid.

 $CO_2 + H_2O \Longrightarrow H_2CO_3$  ( $CO_2$  is called carbonic anhydride.) Carbonic acid is known only in solution and has never been isolated in free state.

The carbonic acid is a dibasic acid and it forms two series of salts by replacement of one or both the hydrogen atoms.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

- (a) Acid salts, are also called bicarbonates or hydrogen carbonates. These contain  $HCO_3^-$  ions.
- (b) Normal salts, are also called carbonates. These contain  $CO_3^{2-}$  ions.

The metallic carbonates or bicarbonates are prepared by following methods:

(i) By passing CO<sub>2</sub> through the solution of base:

$$2\text{NaOH} + \text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$

$$\downarrow^{\text{CO}_2 + \text{H}_2\text{O}}$$

$$\text{NaHCO}_3$$

$$\text{Ca(OH)}_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$

$$\downarrow^{\text{CO}_2 + \text{H}_2\text{O}}$$

$$\downarrow^{\text{CO}_2 + \text{H}_2\text{O}}$$

$$\text{Ca(HCO}_3)_2$$

(ii) By reacting basic oxides and CO2:

$$K_2O + CO_2 \longrightarrow K_2CO_3$$
  
 $Na_2O + CO_2 \longrightarrow Na_2CO_3$ 

(iii) By double decomposition, i.e., by using sodium carbonate :

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$
  
 $BaCl_2 + Na_2CO_3 \longrightarrow BaCO_3 + 2NaCl$ 

**Properties: (i) Solubility:** (a) Except alkali metals carbonates, all other carbonates are insoluble in water.

- (b) The bicarbonates are soluble in water. The bicarbonates of alkali metals are known in solid state while the bicarbonates of alkaline earth metals are only known in solutions.
- (ii) Action of heat: (a) All bicarbonates decompose on heating evolving carbon dioxide. The carbonate formed may further decompose except alkali metal carbonates.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$
  
 $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$ 

- (b) Alkali metal carbonates except Li<sub>2</sub>CO<sub>3</sub> do not decompose on heating.
- (c) All other carbonates decompose on heating with evolution of carbon dioxide.

$$ZnCO_3 \longrightarrow ZnO + CO_2$$
  
 $CaCO_3 \longrightarrow CaO + CO_2$   
 $CuCO_3 \longrightarrow CuO + CO_2$   
 $Ag_2CO_3 \longrightarrow 2Ag + CO_2 + \frac{1}{2}O_2$ 

(iii) Action of acids: Both carbonates and bicarbonates are decomposed by the action of acids with evolution of  $CO_2$  (effervescences).

$$Na_2CO_3 + 2HCI \longrightarrow 2NaCl + H_2O + CO_2$$
  
 $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$   
 $ZnCO_3 + H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$ 

(iv) Action of MgSO<sub>4</sub>: This is the reagent with which carbonates and bicarbonates can be distinguished and tested. Soluble carbonates form an insoluble white precipitate with magnesium sulphate in cold.

$$Na_2CO_3 + MgSO_4 \longrightarrow MgCO_3 + Na_2SO_4$$
  
White ppt.

Bicarbonates do not form any white precipitate with magnesium sulphate in cold. However, when such solution is heated, a white precipitate appears.

(v) Effect of phenolphthalein: Soluble carbonates produce pink colour with phenolphthalein showing higher pH value while bicarbonates do not give pink colour with phenolphthalein.

### 3. Gaseous Fuels

Fuels are the substances which undergo combustion. As a result of their burning, they produce heat energy. During combustion, no undesirable product should be formed. The heat energy production depends on the presence of combustible substances such as carbon, carbon monoxide, carbonous matter, hydrogen, etc., in the fuels. Most common fuels are:

- (a) Solid fuels: Wood, lignite, peat, coke, charcoal, etc.
- **(b) Liquid fuels:** Petroleum products such as petrol, kerosene, spirits, etc.
- (c) Gaseous fuels: Water gas, producer gas, coal gas, oil gas, natural gas, etc.

Characteristics of good fuel: (i) It should have high calorific value.

- (ii) It should yield very little ash content.
- (iii) It should not give any offensive odour or any undesirable product during burning.
- (iv) It's cost of production should be low and it should be easily available.
  - (v) The combustion should be of moderate speed.

**Superiority of gaseous fuels:** Gaseous fuels are the best fuels. The following are the advantages of gaseous fuels over solid and liquid fuels:

- (i) Gaseous fuels leave no ash and there is lesser loss of heat during their combustion.
  - (ii) Gaseous fuels do not produce smoke.
  - (iii) They have high calorific value.
  - (iv) No special devices are required for their combustion.

(v) Gaseous fuels can flow through pipes and can be ignited at the moment's notice at any place where a burner is placed. Some of the important gaseous fuels are discussed below:

### (i) Producer Gas

Producer gas is mainly a mixture of carbon monoxide and nitrogen. It is prepared by the incomplete combustion of coal, coke or charcoal. The combustion is done in restricted supply of air.

$$\begin{array}{c} C + O_2 \longrightarrow CO_2 + 97.7 \text{ kcal} \\ CO_2 + C \longrightarrow 2CO - 38.3 \text{ kcal} \\ \hline 2C + O_2 \longrightarrow 2CO + 59.4 \text{ kcal} \end{array}$$

Initially, carbon dioxide is the main product but when it rises through the bed of coal, it combines with carbon, provided the temperature is 1000°C, forming carbon monoxide. Thus, heat is generated during its preparation. This heat can also be utilised if producer gas is generated on the spot and used while still hot.

Producer gas is poisonous, heavier than air and insoluble in water. It has a low calorific value. The CO burns and converted into  $\mathrm{CO}_2$  in air producing heat energy. The low calorific value (103 B.Th.U. per cubic ft) is due to the presence of large proportion of nitrogen in it. It is mainly used as a gaseous fuel in open hearth furnace in the manufacture of steel and glass. It is also used to heat coke ovens for the manufacture of coal gas.

## (ii) Water Gas

Water gas is mainly a mixture of CO and H<sub>2</sub>. It is made by blowing steam through the layers of incandescent (red hot) coal. The efficient working temperature is 1000–1400°C.

$$C + H_2O \longrightarrow CO + H_2 - 28 \text{ kcal}$$

Due to endothermic nature of this reaction, the coal cools down after sometime and the formation of carbon dioxide starts at low temperature. To check this formation, the current of steam is replaced by a blast of air. This raises the temperature of coal and steam is readmitted. In general, water gas consists of 40 volumes of CO, 50 volumes of  $H_2$ , 5 volumes of

The calorific value of water gas is fairly high (310 B.Th.U. per cubic ft). The calorific value of water gas is increased by carburetting, *i.e.*, adding gaseous hydrocarbons obtained by cracking of petroleum oils.

Water gas is used as a fuel and for the manufacture of hydrogen. It is also used for lighting purposes and in the manufacture of methyl alcohol. The flame of water gas is short and hot, it is thus used for welding purposes.

## (iii) Coal Gas

Coal gas is a mixture of hydrogen, methane, carbon monoxide, ethylene, acetylene, carbon dioxide, nitrogen and oxygen. It is a good gaseous fuel as it contains about 95% combustible gases. The calorific value of coal gas is 450–650 B.Th.U. per cubic ft. The average composition of coal gas by volume is:

Hydrogen	56%;	Ethylene, acetylene	2.5%
Methane	22.8%;	Carbon dioxide	1.3%
Carbon monoxide	10.9%;	Oxygen	0.5%
Nitrogen	5.0%		

Hydrogen, methane and carbon monoxide are non-illuminating but heat producing constituents. The unsaturated hydrocarbons produce illumination. Nitrogen, carbon dioxide and oxygen are present as impurities.

Coal gas is obtained by destructive distillation of coal at about 1000°C. For this purpose, coal is heated at 1000–1100°C in a large fire-clay retorts. The products of decomposition are: (i) coal gas (ii) coke (iii) coal tar (iv) ammonical liquor. One ton of bituminous coal gives about 13000 cubic ft of coal gas.

**Uses:** It is used:

- (i) as a fuel in the household and in metallurgical operations.
- (ii) in providing inert atmosphere in certain chemical processes.
  - (iii) in smelting of metals and alloys.
  - (iv) as a reducing agent.
  - (v) as an illuminating gas.

### (iv) Oil Gas

Oil gas is obtained by cracking of kerosene. It is a mixture of lower hydrocarbons, mainly CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, etc.

A thin stream of oil is allowed to drop on the red hot surface of an iron retort. The kerosene is broken down into gaseous hydrocarbons.

$$C_{16}H_{34} \longrightarrow 6CH_4 + 2C_2H_4 + C_2H_2 + 4C$$

The gas mixture is passed through hydraulic main to remove tar and soluble impurities and then collected in gas holder.

Oil gas is generally used in laboratories.

Petrol gas is a mixture of petrol vapours and air. It is obtained by passing air through petrol (solvent oil). Nowadays, petrol gas is used in the laboratories instead of oil gas.

## (v) Natural Gas

Natural gas is found in regions rich in petroleum. The gas consists of chiefly methane. The approximate composition of a sample of natural gas is given below:

The composition may vary from place to place. Natural gas from certain regions has been found to have sufficient proportion of helium. Chief use of natural gas is as a fuel. It is also used for the production of hydrogen, carbon black and various petrochemicals.

## (vi) Liquefied Petroleum Gas (LPG)

Liquid or liquefied petroleum gas (LPG) is a clean burning gaseous fuel which contains  $C_3$  and  $C_4$  hydrocarbons of the alkane and alkene series. LPG contains hydrocarbons of such volatility that can exist as gases under normal temperature and atmospheric pressure, but can be easily liquefied under high pressure, *i.e.*, the critical temperature of the gaseous mixture (LMP) is nearly equal to room temperature. The main constituents of LPG are n-butane, isobutane, butene and propane.

LPG is generally isolated either from **natural gas** or from the **cracking units of petroleum refineries.** During fractional distillation of crude petroleum, the gases collected at the top of the fractionating tower which do not condense at all (hydrocarbons having low boiling points such as methane, ethane, propane, butanes, etc.) are used for making LPG. The mixture of lower hydrocarbons is condensed under high pressure in refrigeration units. However, traces of sulphur containing compounds such as ethyl mercaptan (C<sub>2</sub>H<sub>5</sub>SH) or methyl mercaptan (CH<sub>3</sub>SH) are deliberately added in order to detect any dangerous leakage from the gas cylinder.

The density of LPG is about 0.55g mL<sup>-1</sup> and is colourless, taşteless, odourless and non-toxic in nature. However, life is not possible in its gaseous atmosphere due to lack of oxygen, *i.e.*, it is suffocating in nature. In gaseous state it is twice heavy as air. It is highly inflammable and produces heat energy on combustion in air.

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O + \text{Heat}$$
 
$$C_4H_{10} + \left(\frac{13}{2}\right)O_2 \longrightarrow 4CO_2 + 5H_2O + \text{Heat}$$

The average calorific value of LPG is 55 kJg<sup>-1</sup> or 29780 kcal/m<sup>3</sup>. LPG is used as a domestic fuel, direct motor fuel, laboratory gas and a source of petrochemicals. About 80% LPG is used nowadays in India as a domestic fuel (Cooking gas). Domestic installation consists of a LPG cylinder, pressure regulator, rubber tubing and a hot plate. On opening the cylinder valve with the help of pressure regulator, the pressure inside the cylinder is reduced causing LPG liquid to vaporise into gas. The gas through rubber tube reaches the burner of the hot plate where it is mixed with air and burnt.

## LPG is the safest fuel but requires certain simple precautions in day to day use.

- (i) As LPG is heavier than air and as such, it travels towards floor, so it is important that the flame should be at higher level than cylinder. Thus, it is recommended that hot plate level should be above cylinder height.
- (ii) There should be no electrical appliances like fridge in the kitchen which can cause electric spark during switch on or off.

- (iii) In case of smell of gas inside the kitchen, no flame should be produced and no electric switch be touched.
- (iv) The LPG cylinder should never be stored in cupboard.
- (v) Kitchen should be airy.
- (vi) After cooking is over, the pressure regulator should be turned off.

## LPG is an ideal fuel in modern living. The main advantages of LPG are :

- (a) It gives instant flame by just lighting a match box or lighter.
- (b) It gives instant heat, there is no need to wait for appliances to warm up.
- (c) It gives correct amount of heat required, as the size of the flame can be adjusted.
- (d) It gives comfort because cooking is quicker and the kitchen does not get heated or get dirty like other fuels.
- (e) It is much cheaper than other fuels.
- (f) It is easy to store. The cylinder occupies very little space. LPG connections can be transferred from one place to another.

## (vii) Gobar Gas or Bio-gas

The mixture of gases that can burn and produce heat energy, which is emitted from places where organic wastes (like animal dung, human excreta, vegetable waste, leaves, etc.) decay out of contact of air is called bio-gas or gobar gas.

Its main constituent is methane (60–70%). Other gases present are CO, H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub>, etc. Bio-gas is combustible. It gives a blue flame with a lot of heat which may be used for cooking, lighting and as a fuel for petrol and diesel engines.

Organic waste is made to decay out of contact of air when bio-gas is produced. This process is called **anaerobic fermentation**. The waste that remains after fermentation called **slurry** is a very good fertilizer as the bacteria add a lot of nitrogen to the waste during fermentation, thus improving the quality of the fertilizer.

Bio-gas has become a very practical alternative energy resource in several rural areas of the country.

## 4. Carbides

Carbides are binary compounds of carbon with elements of lower or about equal electronegativity. Carbides are classified into three types on the basis of chemical bonding. These are salt-like carbides, covalent carbides and interstitial or alloy like carbides. Carbides are generally prepared by heating the element or its oxide with carbon or hydrocarbon at very high temperatures.

$$\begin{array}{c} Ba + 2C \longrightarrow BaC_2 \\ 2Li + 2C \longrightarrow Li_2C_2 \\ CaO + 3C \longrightarrow CaC_2 + CO \\ 4Li + C_2H_2 \longrightarrow Li_2C_2 + 2LiH \end{array}$$

**Salt-like carbides:** These carbides are formed by the metals of groups IA, IIA and IIIA (except boron), coinage metals, zinc, cadmium and some lanthanides. Depending on

the nature of the hydrocarbon formed during hydrolysis by water or dilute HCl, the ionic carbides can be further classified into the following types:

- (i) Acetylides: These are the ionic carbides which yield acetylene on hydrolysis. These are regarded as derivatives of acetylene and are thus called acetylides. The alkali metals and copper, silver and gold form  $M_2C_2$  type compounds. The alkaline earth metals, zinc and cadmium give  $MC_2$  type carbides. These carbides are believed to contain  $[C = C]^{2-}$  groups. Two types of crystal structures characterise these carbides. Both are tetragonal and are derived from sodium chloride structure by replacement of  $Cl^-$  ions by  $C_2^{2-}$  ions.
- (ii) Methanides: These carbides evolve methane on hydrolysis. These are regarded as derivatives of methane and are called methanides. Al<sub>4</sub>C<sub>3</sub>, Be<sub>2</sub>C, Mn<sub>3</sub>C,etc., are some examples of methanides. These contain C<sup>4-</sup> groups.
- (iii) Allylides: These carbides evolve allylene (methyl acetylene) on hydrolysis. The only example of this type is  $Mg_2C_3$ . It contains  $C_3^{4-}$  discrete groups.

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3 \longrightarrow C \equiv CH$$
Propyne

(iv) Mixed carbides: These carbides yield a mixture of hydrocarbons on hydrolysis. Carbides of iron group,  $UC_2$  and  $ThC_2$  belong to this class.

**Covalent carbides:** The only true covalent carbides are those of silicon (SiC carborundum) and boron (B<sub>4</sub>C and B<sub>13</sub>C<sub>2</sub>). These are chemically inert and extremely hard materials. On account of hardness, these carbides are used as abrasives.

Silicon carbide is produced by heating quartz or sand with an excess of coke in an electric arc furnace.

$$SiO_2 + 3C \xrightarrow{2000-2500^{\circ}C} SiC + 2CO\uparrow$$

**Metallic or interstitial carbides:** In these carbides, small carbon atoms occupy interstitial positions in the crystal lattices of the metals. These are of two types: MC (M = Ti, Zr, Hf, V, Nb, Ta, Mo, W) and  $M_2C$  (M = V, Mo and W). These carbides possess metallic lustre, high electrical conductivity and are chemically inert. These are extremely hard like diamond and possess very high melting points.

- **Uses:** (i) Calcium carbide is used to prepare acetylene. Acetylene is the starting material for many organic compounds. It is also used for production of oxy-acetylene flame employed for welding purposes.
- (ii) SiC, being hard substance, is used as abrasive. Boron carbide is also used as abrasive and shield from radiations. It is used for the construction of atomic reactors.
- (iii) Carbides which can withstand high temperature are used widely in furnace lining.
- (iv) Tungsten carbide, WC, is used for the manufacture of high speed tools.

## 9.6 SILICON

Silicon is the second most abundant element occurring in the earth's crust (about 28% by weight). Silicon and oxygen make up 75% of the crust of the earth. Unlike carbon, it is never found in free state but always in combined state. It is an important constituent of igneous rocks which consists of silicates of magnesium, aluminium, potassium or iron. Silicon is widely present as silica (SiO<sub>2</sub>) in various forms such as sand, quartz, flint, etc. Silicon dioxide, SiO<sub>2</sub> has a melting point of 1710°C.

Silicon is obtained by the reduction of silica. It exists in two allotropic forms: (a) amorphous and (b) crystalline. The amorphous variety is obtained by heating dry powdered silica with magnesium.

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

The crystalline variety is obtained by heating a finely powdered sand or quartz with carbon in an electric furnace. A small amount of iron is added to prevent the formation of carborundum (SiC).

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

High purity silicon can be prepared by reducing SiCl<sub>4</sub> with magnesium.

$$SiCl_4 + 2Mg \longrightarrow Si + 2MgCl_2$$

The magnesium chloride, being water soluble, is then washed away from the silicon. The final purification of silicon takes place by **zone-refining.** 

Amorphous silicon is chemically more reactive than crystalline silicon. Amorphous silicon is a brownish powder. It burns brilliantly in oxygen and ignites spontaneously in fluorine.

$$Si + O_2 \longrightarrow SiO_2$$
  
 $Si + 2F_2 \longrightarrow SiF_4$ 

It decomposes steam at red heat. It dissolves in the mixture of HNO<sub>3</sub> and HCl. However, it dissolves readily in alkalies.

$$Si + 2H2O \longrightarrow SiO2 + 2H2$$

$$Si + 2KOH + H2O \longrightarrow K2SiO3 + 2H2$$

$$Na2CO3 + Si \longrightarrow Na2SiO3 + C$$

It combines with certain metals forming silicides.

$$2Mg + Si \longrightarrow Mg_2Si$$

When amorphous silicon is strongly heated, it fuses and on cooling solidifies to the crystalline form. It is very hard crystalline silicon, does not burn in oxygen but it readily combines with fluorine. It dissolves in mixture of HNO<sub>3</sub> and HF. When fused with alkali, it gives a silicate.

$$Na_2CO_3 + Si \longrightarrow Na_2SiO_3 + C$$

Silicon is used in the manufacture of certain alloys such as ferrosilicon, silicon bronze, manganese silicon bronze, etc. These alloys possess high strength and hardness and resistant to the attack of acids.

One outstanding property of silicon in a high state of purity is its electrical conductivity. It acts as a **semiconductor**, *i.e.*, it does not conduct electricity until a cartain electric voltage is applied, but beyond that it conducts moderately. Its conductivity

properties can be changed by a process known as **doping**, *i.e.*, placing other atoms in a crystal of pure silicon.

The excesses (*n*-type) and deficiencies (*p*-type) of electrons result from inserting arsenic and boron atoms respectively in the place of silicon atoms in the crystalline structure. In 1947, an electrical device called the **transistor** was invented. The simplest device used layers of *n*-*p*-*n* or *p*-*n*-*p*-doped silicon. The most revolutionary application of silicon's semiconductor properties has been in the design of **integrated circuits**, computer memories and even whole computers called **microprocessors** on tiny chips of silicon. These are used in calculators, cameras, watches, toys, cardiac pacemakers and many other products.

## 9.7 COMPOUNDS OF SILICON

## 1. Carborundum (Silicon Carbide), SiC

It is obtained when a mixture of sand, carbon, common salt and saw dust is strongly heated in an electric furnace.

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Salt is added to act as flux and saw dust makes the mass porous. Two carbon rods connected by a thin carbon core act as electrodes in the furnace. Carborundum is formed round the central core of carbon. It is crushed, washed with H<sub>2</sub>SO<sub>4</sub>, NaOH, H<sub>2</sub>O and then dried.

**Properties:** (i) Pure carborundum is colourless but commercial samples possess yellow, green or blue colour.

- (ii) It is very hard mass. However, its hardness is less than diamond.
- (iii) It is chemically inert and resists the attack of almost all the reagents except fused caustic soda. The fused alkali dissolves it in presence of air.

$$4\text{NaOH} + \text{SiC} + 2\text{O}_2 \longrightarrow \text{Na}_2\text{SiO}_3 + \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$$
 Its structure is similar to diamond.

**Uses:** It is used as an abrasive instead of emery. It is used to make grind-stones, knife sharpeners, etc.

## 2. Sodium Silicate, Na<sub>2</sub>SiO<sub>3</sub> (Water Glass)

It is commercially called water glass. Chemically it is sodium metasilicate containing an excess of silica. Its composition may vary from Na<sub>2</sub>SiO<sub>3</sub>·SiO<sub>2</sub> to Na<sub>2</sub>SiO<sub>3</sub>·3SiO<sub>2</sub>.

It is obtained by fusing soda ash (Na<sub>2</sub>CO<sub>3</sub>) with pure sand at a high temperature.

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$

The resulting mass is extracted with water and the solution is evaporated to get a syrupy mass known as water glass.

**Properties:** It is soluble in water. The solution is alkaline due to hydrolysis.

$$Na_2SiO_3 + 2H_2O \implies 2NaOH + H_2SiO_3$$

If in a solution of sodium silicate of density 1.1, some coloured salts like cobalt nitrate, nickel chloride, ferrous

sulphate, copper sulphate, etc., are placed and whole solution is left as such for a night, beautiful hollow tubes of metallic silicate gels possessing different colours shoot up from these crystals and look like plants. This is called **silica garden** or **chemical garden**.

Uses: It is used:

- (a) in fire proofing of wood and textiles.
- (b) as a preservative for eggs.
- (c) as an adhesive cement for joining pieces of china clay.
- (d) in the soap industry as a filler for a cheaper variety of soap.
- (e) in paint industry and calico printing.
- (f) for making silica gel, SiO<sub>2</sub>·xH<sub>2</sub>O. When a solution of Na<sub>2</sub>SiO<sub>3</sub> is acidified with HCl, a gelatinous precipitate of silicic (H<sub>2</sub>SiO<sub>3</sub>) acid is slowly formed.

$$Na_2SiO_3 + 2HCl \longrightarrow 2NaCl + H_2SiO_3$$

If most of the water is carefully removed, the jelly like precipitate of H<sub>2</sub>SiO<sub>3</sub> is converted into a solid product which is called silica gel. It possesses excellent absorption property of gases and vapours.

#### 3. Silicones

These are organosilicon polymers containing Si—O—Si linkages. These are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation. The alkyl or aryl substituted chlorosilanes are prepared by the reaction of Grignard reagent and silicon tetrachloride.

$$RMgCl + SiCl_4 \longrightarrow R - SiCl_3 + MgCl_2$$
Grignard reagent

$$2RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$$

$$3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$$

R stands for 
$$-CH_3$$
,  $-C_2H_5$  or  $-C_6H_5$  groups.

Hydrolysis of substituted chlorosilanes yield corresponding silanols which undergo polymerisation.

Polymerisation of dialkyl silandiol yields linear thermoplastic polymer.

Polymerisation continues on both the ends and thus chain increases in length.

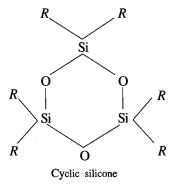
RSiCl<sub>3</sub> on hydrolysis gives a cross linked silicone. The formation can be explained in three steps:

Cyclic (ring) silicones are formed when water is eliminated from the terminal —OH groups of linear silicones.

R

Cross linked silicone

R



 $R_3$ SiCl on hydrolysis forms only a dimer

$$R_3$$
Si O  $\stackrel{\cdot}{H} + \stackrel{\cdot}{O}\stackrel{\cdot}{H}$  Si $R_3 \longrightarrow R_3$ Si—O—Si $R_3$ 

**Properties:** (i) The lower silicones are oily liquids but higher members containing long chains or ring structures are waxy and rubber like solids.

- (ii) Silicones are stable towards heat.
- (iii) Chemical reagents have no action on silicones.
- (iv) These are non-toxic.
- (v) Viscosity of silicone oils remains the same at different temperatures.
  - (vi) Silicones are good electrical insulators.
  - (vii) These are water repellants.

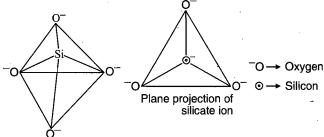
**Uses:** (i) Silicone oils are used for high temperature oil baths, high vacuum pumps and low temperature lubrication.

- (ii) These are used in making water-proof cloth and paper by exposing cloth or paper to the silicone vapour.
- (iii) These are used as insulating materials for electric motors and other electrical appliances.
- (iv) These are mixed with paints and enamels to make them resistant to the effects of high temperature, sunlight, chemicals and damp.
- (v) These are used in making vaseline like greases which are used as lubricants in aeroplanes.
- (vi) Silicone-rubbers are useful as they retain their elasticity over a range of temperatures.

#### 4. Silicates

Silicates are metal derivatives of silicic acid, H<sub>4</sub>SiO<sub>4</sub> or Si(OH)<sub>4</sub>. Silicates are formed by heating metal oxide or metal carbonates with sand, *e.g.*,

$$Na_2CO_3 - \xrightarrow{Fused with sand} Na_4SiO_4$$
,  $Na_2(SiO_3)_n$ , etc.

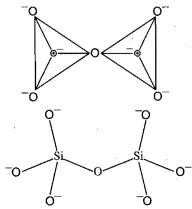


Silicates have basic unit of  $SiO_4^{4-}$ , each silicon atom is bonded with four oxide ions tetrahedrally.

There are following types of silicates:

- (i) Orthosilicates: These silicates contain single discrete unit of  $SiO_4^{4-}$  tetrahedra,
- e.g., Zircon ZrSiO<sub>4</sub>; Forsterite or Olivine Mg<sub>2</sub>SiO<sub>4</sub> Phenacite Be<sub>2</sub>SiO<sub>4</sub>; Willemite Zn<sub>2</sub>SiO<sub>4</sub>
- (ii) Pyrosilicates: These silicates contain two units of SiO<sub>4</sub><sup>4</sup> joined along a corner containing oxygen atom. These are also called as island silicates.

Pyrosilicate ion Si<sub>2</sub>O<sub>7</sub><sup>6-</sup>,



e.g., Thortveitite

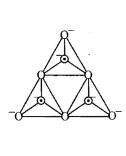
 $Sc_2(Si_2O_7);$ 

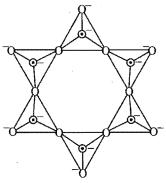
Hemimorphite

 $Zn_3(Si_2O_7)Zn(OH)_2 \cdot H_2O$ 

(iii) Cyclic structure: Cyclic or ring silicates have general formula  $(SiO_3^{2-})_n$  or  $(SiO_3)_n^{2n-}$ .

Structure and example of cyclic silicates containing  $Si_3O_9^{6-}$  and  $Si_6O_{18}^{12-}$  ions are given below:

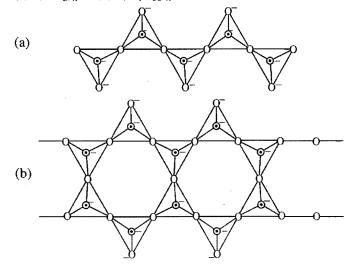




e.g., Beryl Be<sub>3</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>; Benitoite BaTiSi<sub>3</sub>O<sub>9</sub>
Wollastonite Ca<sub>3</sub>Si<sub>3</sub>O<sub>9</sub>; Catapleite Na<sub>2</sub>ZrSi<sub>3</sub>O<sub>9</sub>·2H<sub>2</sub>O

(iv) Chain silicates: Chain silicates are formed by sharing two oxygen atoms by each tetrahedra. Anions of chain silicate have two general formulae,

(a)  $(SiO_3)_n^{2n-}$  (b)  $(Si_4O_{11})_n^{6n-}$ 

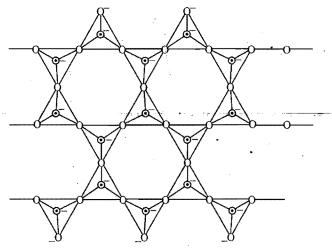


e.g., Synthetic silicates Li<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub>;

 $\begin{array}{lll} \text{Spodumene} & \text{LiAl}(\text{SiO}_3)_2; \\ \text{Jadeite} & \text{NaAl}(\text{SiO}_3)_2; \\ \text{Enstatite} & \text{MgSiO}_3; \\ \text{Diopside} & \text{CaMg}(\text{SiO}_3)_2; \\ \end{array}$ 

Tremolite  $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$ 

(v) Two dimensional sheet silicates: In such silicates, three oxygen atoms of each tetrahedra are shared with adjacent  $SiO_4^{4-}$  tetrahedra, such sharing forms two dimensional sheet structure with general formula  $(Si_2O_5)_n^{2n-}$ .



e.g., Talc  $Mg(Si_2O_5)_2Mg(OH)_2$ Kaolin  $Al_2(OH)_4(Si_2O_5)$ 

(vi) Three dimensional sheet silicates: These silicates involve all four oxygen atoms in sharing with adjacent SiO<sub>4</sub><sup>4</sup> tetrahedra.

e.g., Quartz, Tridymite, Crystobalite, Feldspars, Zeolites and Ultramarines.

Zeolites are a class of three dimensional aluminosilicates. They carry a negative charge on aluminosilicate framework which is compensated by neighbouring alkali-metal or alkaline-earth cations. They possess open structures consisting of polyhedra cavities of uniform size and shape. Most zeolites (natural or synthetic) accommodate water molecules in their cavities, where they provide a mobile phase for the migration of the charge-compensating cations. This enables zeolites to serve as ion - exchange materials and is the key to their ability to soften water.

When hard water is passed through a column packed with a zeolite, the calcium and magnesium ions exchange with the sodium ions,

$$2\text{NaZ}(s) + \text{Ca}^{2+}(aq.) \Longrightarrow \text{CaZ}_2(s) + 2\text{Na}^+(aq.)$$

When the ion exchange capacity of the zeolite is exhausted, this reaction can be reversed by passing a concentrated solution of sodium chloride through the zeolite to regenerate it in the sodium form.

#### 👼 5. Glass

Glass is a transparent or translucent amorphous supercooled solid solution of silicates and borates. The most common silicates present are those of potassium, calcium and lead. Its composition is variable as it is not a true compound.

An approximate formula for ordinary glass may be given as,  $R_2O \cdot MO \cdot 6SiO_2$ 

where R = Na or K and M = Ca, Ba, Zn or Pb.

SiO<sub>2</sub> may be replaced by Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>. When glass is heated, it does not melt at a fixed temperature. However, it gradually softens and can be moulded into any desired shape. It is the property of glass which makes it a useful material for making articles of different shapes. Glass melts into a liquid at a very high temperature.

**Raw materials:** Following are the main raw materials used in the manufacture of glass:

- (a) Acidic oxides: A number of acidic oxides are used. The choice depends upon the quality of glass to be manufactured.
- (i) Silica: Sand of uniform size is used, *i.e.*, neither too fine nor too coarse. Fine variety makes the reaction violent while coarse variety slows down the reaction. It should be free from iron oxide and organic matter.
- (ii) Boron trioxide, B<sub>2</sub>O<sub>3</sub>: This is introduced in the form of boric acid or borax. It is used when a glass of low coefficient of expansion is required.
- (iii) Phosphorus pentoxide, P<sub>2</sub>O<sub>5</sub>: It is introduced in the form of calcium phosphate. It is used when opalescent glass is required.
- **(b) Basic oxides:** One or more of the following basic oxides are used:

Lithium, sodium, potassium, calcium, barium, magnesium, lead and zinc oxides. Sodium is introduced in the form of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), sodium nitrate (NaNO<sub>3</sub>) or sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) and carbon mixture. Potassium is added as potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) or potassium nitrate (KNO<sub>3</sub>). Calcium is added as CaCO<sub>3</sub> or CaO. Barium is put in as BaCO<sub>3</sub>. Magnesium is added as MgCO<sub>3</sub>. Lead oxides are put in as such. Zinc oxide is used when heat resistant glass is to be obtained.

(c) Colouring materials: Coloured glasses are obtained by adding certain metallic oxides or salts in the fused mass. The following is the list of various substances used for imparting a particular colour to the glass.

Substance	Colour imparte
Ferric oxide	Yellow
Chromic oxide	Green
Cobalt oxide	Blue
Selenium metal	Red
Manganese oxide	Purple
Cuprous oxide	Red
Cadmium sulphide	Yellow
Nickel oxide,	
Cobalt oxide,	Black
Manganese oxide	

**Manufacture:** The raw materials used in the manufacture of glass depend on the variety of glass. For ordinary glass, the raw materials are sand, washing soda and limestone. These are ground separately and mixed in the proper proportion, *i.e.*, in the ratio of 100:35:15. The mixture is known as "batch". Broken glass pieces known as "cullet" are added to the mixture of raw materials. Cullet melts at low temperature and helps in melting the rest of charge at low temperature.

The charge is fused now either in a pot or tank furnace at about 1400°C. This temperature is obtained by burning producer gas. Both the furnaces work on the regenerative system of heat economy. A tank furnace is used where the output expected is large but where the highest quality of glass is desired, the pot furnace is used. In tank furnace, the process is continuous while in pot furnace the process is discontinuous.

**Pot furnace:** A pot is a large monkey shaped crucible of the type given in Fig. 9.6. In a pot furnace a number of such pots are arranged in a circle. These are heated by burning producer gas.

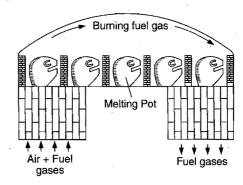


Fig. 9.6 Pot furnace

**Tank furnace:** It is a large rectangular clay tank in which raw materials are fused. It is also heated by producer gas (Fig. 9.7).

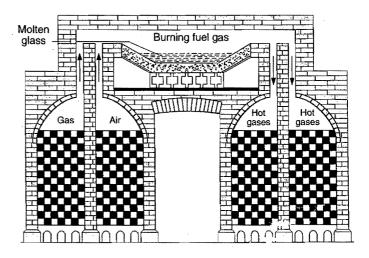


Fig. 9.7 Tank furnace

The free silica decomposes the carbonates, setting the evolution of CO<sub>2</sub>.

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$
  
 $CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$ 

At 1400°C silica also dissolves in the silicates of sodium and calcium.

$$Na_2SiO_3 + CaSiO_3 + 4SiO_2 \longrightarrow \underbrace{Na_2SiO_3 \cdot CaSiO_3 \cdot 4SiO_2}_{Glass}$$

The heating is continued till bubbles of CO<sub>2</sub> no longer rise and the mass melts to a clear liquid. The clear viscous liquid is then poured into moulds or stamped with dies to produce desired articles.

**Annealing:** The glass if cooled rapidly becomes brittle and fragile. The articles of glass are cooled neither very slowly nor very rapidly. These are made to pass through a long tunnel like furnace which is very hot at the mouth end and very cold at the tail end, *i.e.*, the articles are cooled gradually during passage through the tunnel. This process is termed as annealing and takes several days for completion.

The articles so cooled require some finishing such as cutting, grinding, polishing, etc. Only the finished products are sold in the market.

## Varieties of glass:

By varying the composition of batch, several varieties of glass are obtained. Some of the varieties are the following:

- (i) Soda glass or soft glass: It is a mixture of sodium and calcium silicates. It is a cheap variety. It softens at a comparatively low temperature and can be easily shaped into different forms. It is used in making glass tubes, window panes, bottles, dishes, etc.
- (ii) Potash glass or hard glass: It is a mixture of potassium and calcium silicates. It fuses with difficulty. It is more resistant to the action of water and acids. It is used for making hard glass apparatus.
- (iii) Flint glass: It is a mixture of potassium and lead silicates. It has a very high refractive index and is used for making electric bulbs and optical instruments.
- (iv) Jena glass: It is a mixture of zinc and barium borosilicates. It is resistant to heat, shock and common reagents. It is used for making good quality of glasswares.
- (v) Pyrex glass: It is a mixture of zinc, barium borosilicates and alumino silicates. It is similar to jena glass in properties. It can withstand sudden changes in temperature and is highly suitable for laboratory glassware and oven glassware. Its approximate composition is: silica 80%, Na<sub>2</sub>O 4%, CaO 0.5%, K<sub>2</sub>O 0.5%, B<sub>2</sub>O<sub>3</sub> 12%, Al<sub>2</sub>O<sub>3</sub> 3%.
- (vi) Crooke's glass: It is a special type of glass containing cerium oxide. It does not allow the passage of ultraviolet rays. It is used for making lenses.

### Etching of glass:

Glass is attacked by hydrofluoric acid. This property is used in the etching of glass.

The glass to be etched is coated with a thin layer of wax and the design to be produced is scratched with a needle or stylus. An aqueous solution of hydrofluoric acid is applied to the exposed part. After sometime it is placed in water and wax is removed from the surface. The marks are engraved on the exposed parts.

## 9.**8** TIN

**Occurrence:** Tin does not occur free in nature. The most important ore is cassiterite, SnO<sub>2</sub>, which is also known as tin stone. The ore is usually associated with siliceous matter, tungstates of iron (FeWO<sub>4</sub>) and manganese (MnWO<sub>4</sub>). It also exists along with the pyrites of copper, iron and zinc.

**Extraction:** Tin is extracted from cassiterite ore. The extraction involves the following steps:

- (a) Concentration: The ore is crushed and powdered. It is washed with running water which removes lighter siliceous matter. Iron tungstate is removed by electromagnetic separator. The ore is now roasted in a current of air to remove sulphur and arsenic as  $SO_2$  and  $As_2O_3$ , respectively.
- **(b) Smelting:** The roasted ore is mixed with about one fifth its mass of powdered anthracite (carbon) and a little limestone (flux). The mixture is subjected to heat in a reverberatory furnace when tin oxide is reduced to tin metal. The liquid metal is drawn off from the furnace.

$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

The crude tin metal contains a number of impurities. It is further purified by liquation and poling. The crude metal is heated gently on the sloping hearth of reverberatory furnace. The tin metal flows down leaving behind iron, copper, tungsten, etc. The molten metal is now stirred with a green wood pole whereby impurities like S, As are oxidised, and any tin oxide formed is reduced by the hydrocarbons of wood.

**Properties:** (i) Tin is a silvery white metal. It melts at 232°C and boils at 2270°C. It is not affected by air.

- (ii) It is malleable and ductile but at 200°C, it becomes brittle and can be powdered.
- (iii) It produces a peculiar sound whenever it is bent. The cracking sound is known as *tincry*.
- (iv) It exists in three allotropic forms. White tin is the common and most stable.

Density Grey 
$$\frac{18^{\circ}\text{C}}{5.74}$$
 White  $\frac{170^{\circ}\text{C}}{7.32}$  Rhombic 6.55

The conversion of white tin to grey tin in cold countries is accompanied by decrease in density, *i.e.*, increase in volume. It is very brittle and easily comes into powdered form. This is termed as *tin disease* or *tin pest* or *tin plague*.

(v) Tin is much less reactive than the metals of group IA, IIA and IIIA. When heated in presence of oxygen at 1500-1600°C, it burns with bright flame forming stannic oxide, SnO<sub>2</sub>.

$$Sn + O_2 \xrightarrow{Heat} SnO_2$$

It is not attacked by water. Molten tin decomposes steam with liberation of hydrogen.

(vi) Tin is not attacked by organic acids. This property is utilised for tinning cooking utensils made of copper or brass. It dissolves slowly in dil. HCl but readily in conc. HCl.

$$Sn + 2HCl \longrightarrow SnCl_2 + H_2$$

It dissolves in dil. H<sub>2</sub>SO<sub>4</sub> as well as in conc. H<sub>2</sub>SO<sub>4</sub>.

$$Sn + H_2SO_4(dil.) \longrightarrow SnSO_4 + H_2$$

$$Sn + 4H_2SO_4(conc.) \longrightarrow Sn(SO_4)_2 + 2SO_2 + 4H_2O$$

Dilute HNO<sub>3</sub> dissolves tin with the formation of ammonium nitrate.

$$4[Sn + 2HNO_3 \longrightarrow Sn(NO_3)_2 + 2H]$$

$$HNO_3 + 8H \longrightarrow NH_3 + 3H_2O$$

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Conc. HNO<sub>3</sub> oxidises Sn into metastannic acid.

$$2[2HNO_3 \longrightarrow H_2O + 2NO_2 + O]$$

$$Sn + 2O + H_2O \longrightarrow H_2SnO_3$$

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

(vii) Tin dissolves in hot alkali solutions forming stannates.

$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2$$

(viii) Tin directly combines with halogens and sulphur.

$$Sn + 2Cl_2 \longrightarrow SnCl_4$$
 (Stannic chloride)  
 $Sn + 2S \longrightarrow SnS_2$  (Stannic sulphide)

**Uses:** (i) The metal is extensively used in tinning brass utensils. Organic acids present in the food stuff attack the utensils which are made of copper, brass, etc. This may cause food poisoning. The utensils are protected by tinning, *i.e.*, depositing a thin layer of tin on the surface of utensils. The vessel to be tinned is perfectly cleaned and heated. A pinch of NH<sub>4</sub>Cl is sprinkled to remove the oxide film. A little tin is now fused on the clean surface and then rubbed over with the help of cotton rag to have a uniform layer.

- (ii) It is largely used in forming a protective coating over iron. The process of depositing tin over the sheets of iron or steel is called tin plating. Tin plating is done either mechanically or electrically.
- (iii) Tin in the form of tin foil is used for wrapping cigarettes, confectionary and for making the tooth-paste tubes.
  - (iv) Tin amalgam is used in making mirrors.
  - (v) It is used for making useful alloys.

Name	Composition	Uses
(i) Solder	Sn 67%, Pb 33%	in soldering
(ii) Rose metal	Sn 28%, Pb 22%, Bi 50%	for electric fuses
(iii) Bronze	Cu 75-90%, Sn 25-10%	for utensils, statues
	•	and coils
(iv) Bell metal	Cu 80%, Sn 20%	bells and gongs
(v) Type metal	Sn 3%, Pb 82%, Sb 15%	printing types
(vi) Britannia metal	Sn 86%, Sb 12%, Cu 2%	cheap table ware

## 9.9 COMPOUNDS OF TIN

#### 1. Stannous Oxide, SnO

**Preparation:** (a) It is prepared from stannous chloride by following methods.

(i) Sodium hydroxide is added to stannous chloride. The stannous hydroxide thus formed is heated in an atmosphere of CO<sub>2</sub> when stannous oxide is formed.

$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$$
  
 $Sn(OH)_2 \xrightarrow{CO_2} SnO + H_2O$ 

(ii) A mixture of solid stannous chloride and sodium carbonate is heated in atmosphere of CO<sub>2</sub>, when stannous oxide is formed.

$$SnCl_2 + Na_2CO_3 \longrightarrow SnO + CO_2 + 2NaCl$$

(b) It may also be prepared by heating stannous oxalate in absence of air.

$$Sn(COO)_2 \longrightarrow SnO + CO + CO_2$$

**Properties:** (i) It is a dark grey or black powder. It is insoluble in water.

(ii) It burns in air with incandescence forming stannic oxide, SnO<sub>2</sub>.

$$2SnO + O_2 \longrightarrow 2SnO_2$$

(iii) It is an amphoteric oxide. It dissolves both in acids and alkalies.

$$\begin{array}{c} SnO + 2HCl \longrightarrow SnCl_2 + H_2O \\ & Stannous \\ & chloride \\ SnO + 2NaOH \longrightarrow Na_2SnO_2 + H_2O \\ & Sod. \ stannite \end{array}$$

Stannites are known only in aqueous solutions. Stannites absorb oxygen from air and oxidised to stannates which are stable in nature.

$$2Na_2SnO_2 + O_2 \longrightarrow 2Na_2SnO_3$$
  
Sod. stannate

## 2. Stannic Oxide, SnO<sub>2</sub>

It is found in nature as cassiterite or tin stone.

**Preparation:** It may be prepared by heating tin in air or by heating metastannic acid which is obtained by reacting tin with concentrated nitric acid.

$$Sn + O_2 \longrightarrow SnO_2$$
  
 $Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O_3$ 

$$H_2SnO_3 \longrightarrow SnO_2 + H_2O$$
  
Metastannic acid

**Properties:** It is a white powder, insoluble in water. It is somewhat unreactive. However, it dissolves in conc. H<sub>2</sub>SO<sub>4</sub> forming stannic sulphate.

$$SnO_2 + 2H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2H_2O$$

When the solution is diluted, stannic oxide is reprecipitated.

$$Sn(SO_4)_2 + 2H_2O \longrightarrow SnO_2 + 2H_2SO_4$$

It readily dissolves in alkalies forming stannates.

$$SnO_2 + 2KOH \longrightarrow K_2SnO_3 + H_2O$$

Stannates are used as mordants in dyeing. It is used in the manufacture of pottery and glass in the form of white glazes.

## 3. Stannous Chloride, SnCl<sub>2</sub>

**Preparation:** (i) Hydrated stannous chloride SnCl<sub>2</sub>·2H<sub>2</sub>O is prepared by dissolving tin in hot concentrated hydrochloric acid and subjecting the solution to crystallisation.

$$Sn + 2HCl \longrightarrow SnCl_2 + H_2$$

Hydrated stannous chloride consists of two molecules of water as water of crystallisation, i.e., SnCl<sub>2</sub>·2H<sub>2</sub>O.

Anhydrous salt cannot be obtained by heating the hydrated salt as it undergoes hydrolysis and a white solid of tin hydroxy chloride is formed.

$$SnCl_2 \cdot 2H_2O \longrightarrow Sn(OH)Cl + HCl + H_2O$$

(ii) Anhydrous stannous chloride is formed when dry HCl gas is passed over hot tin.

$$Sn + 2HCl (gas) \longrightarrow SnCl_2 + H_2$$

It can also be obtained when a mixture of Sn and calculated quantity of mercuric chloride is heated.

$$Sn + HgCl_2 \longrightarrow SnCl_2 + Hg$$

**Properties:** (i) It is a white crystalline solid. It is soluble in water, alcohol and ether.

- (ii) In water, it is soon hydrolysed. However in presence of HCl (acid), hydrolysis is reversed.
- (iii) It forms a white precipitate with alkalies. The precipitate of stannous hydroxide, however, dissolves in excess of alkali.

$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$$
  
 $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$   
Sodium stannite

(iv) It forms a dark brown precipitate of stannous sulphide on passing H<sub>2</sub>S through its solution. The precipitate dissolves in yellow ammonium sulphide.

$$\begin{array}{c} SnCl_2 + H_2S \longrightarrow SnS + 2HCl \\ SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_3 \\ \text{Yellow ammonium sulphide} & \text{Ammonium thiostannate} \end{array}$$

- (v) It is a strong reducing agent. Few examples are given below:
- (a) It reduces mercuric chloride to mercurous chloride (white ppt.) and finally to metallic mercury (dark grey or black).

$$2HgCl_2 \ + \ SnCl_2 \longrightarrow Hg_2Cl_2 \ + \ SnCl_4$$
 Mercurous chiloride

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

(b) It reduces ferric salts to ferrous salts and cupric salts into cuprous salts.

$$2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$$
  
 $2\text{CuCl}_2 + \text{SnCl}_2 \longrightarrow 2\text{CuCl} + \text{SnCl}_4$ 

(c) It decolourises iodine and thus can be titrated with it.

$$SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI$$

(d) Organic nitro compounds are reduced to amino compounds.

$$C_6H_5NO_2 + 6HCl + 3SnCl_2 \longrightarrow C_6H_5NH_2 + 3SnCl_4+2H_2O$$
Nitrobenzene Aniline

(e) It reduces gold chloride to metallic gold.

$$2AuCl_3 + 3SnCl_2 \longrightarrow \begin{array}{c} 2Au + 3SnCl_4 \\ \text{Colloidal gold} \end{array}$$

SnCl<sub>4</sub> undergoes hydrolysis forming stannic acid which absorbs colloidal particles of gold and thus forms purple of cassius.

Uses: It is used: (i) as a reducing agent.

- (ii) for making purple of cassius. Purple of cassius is used for colouring glass and pottery.
  - (iii) as a mordant in dyeing.

### 4. Stannic Chloride, SnCl<sub>4</sub>

It is prepared by passing dry chlorine over fused tin in a retort. The vapours of stannic chloride are condensed in water cooled receiver.

$$Sn + 2Cl_2 \longrightarrow SnCl_4$$

**Properties:** (i) It is a colourless fuming liquid having disagreeable smell.

- (ii) It is hygroscopic and forms crystalline hydrates containing 3, 5, 6 and 8 molecules of water as water of crystallisation. The pentahydrate SnCl<sub>4</sub>·5H<sub>2</sub>O, is known as "butter of tin" or "oxymuriate of tin".
  - (iii) It is soluble in water in which it undergoes hydrolysis.

$$SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl$$

It is also soluble in organic solvents showing that it is a covalent compound.

(iv) It dissolves in conc. HCl forming chlorostannic acid. In presence of ammonium chloride, it forms ammonium salt of this acid.

$$SnCl_4 + 2HCl \longrightarrow H_2SnCl_6$$
Chlorostannic acid
 $SnCl_4 + 2NH_4Cl \longrightarrow (NH_4)_2SnCl_6$ 
Ammonium chlorostannate

Uses: It is used:

- (i) in pentahydrate form as a mordant and in ammonium chlorostannate form as a mordant for pink dyes.
  - (ii) for fire-proofing cotton.
  - (iii) for increasing the weight of silk.

## 9.10 LEAD OR PLUMBUM

**Occurrence:** Lead is mainly found in the form of sulphide. The ore is called the galena, PbS. It is usually associated with zinc blende, iron pyrites and traces of silver (up to 0.1 %). The lead content in galena ore varies from 6 to 8%. The other less important ores of lead are:

(a) anglesite,  $PbSO_4$  (b) cerussite,  $PbCO_3$  (c) lanarkite,  $PbO \cdot PbSO_4$ .

**Extraction:** Lead is mainly extracted, from galena ore. The extraction involves the following steps:

- (i) Concentration of the ore
- (ii) Reduction
- (iii) Purification
- (i) Concentration: The ore is crushed and sieved. It is submitted to the froth floatation process for concentration.

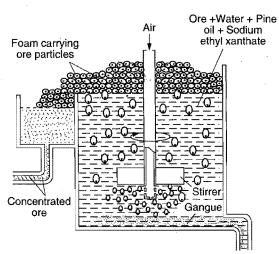


Fig. 9.8 Froth floatation process

The ore is introduced in a large tank containing water to which some pine oil has been added. The mixture is agitated by passing compressed air. The froth is produced which carries away along with it to the surface the ore particles while the gangue settles down at the bottom.

- (ii) Reduction: Two processes are used.
- (a) Air reduction process for ores rich in lead content,
- (b) Carbon reduction process for ores poor in lead content.
- (a) Air reduction process: The concentrated ore is roasted in the reverberatory furnace. The ore is partially oxidised by adjusting the supply of air.

2PbS + 
$$3O_2 \longrightarrow 2$$
PbO +  $2SO_2$   
PbS +  $2O_2 \longrightarrow PbSO_4$ 

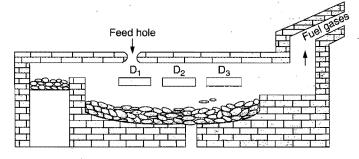


Fig. 9.9 Reverberatory furnace

The temperature of the furnace is raised and air supply is reduced. Some more concentrated galena ore is added. PbS reacts with PbO and PbSO<sub>4</sub> forming lead metal.

$$2PbO + PbS \longrightarrow 3Pb + SO_2$$
  
 $PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2$ 

Thus, roasting and smelting are done in the same furnace at different temperatures.

Molten lead is drawn off from the lower part of the furnace.

(b) Carbon reduction process: The concentrated ore is mixed with some lime and it is then roasted in a sinterer (Fig. 9.10). It is mounted on trunnions for charging and discharging. It is provided with a grating at the bottom and a hood at the top. The air is introduced through grating and is circulated through the charge by applying suction at the top of the hood. PbS oxidised to lead oxide.

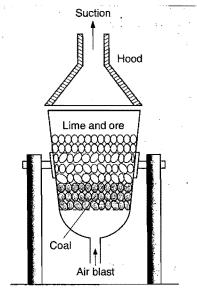


Fig. 9.10 Sinterer

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

Lime serves two purposes:

- (i) It prevents the formation of PbSO<sub>4</sub>.
- (ii) It prevents the formation of PbSiO<sub>3</sub>.

$$[PbSiO_3 + CaO \longrightarrow PbO + CaSiO_3]$$

The sintered ore is crushed into small pieces and mixed with coke and lime. It is fed into a small blast furnace (15–20 feet in height and 3–5 feet in diameter). The following reactions occur in the blast furnace.

$$\begin{array}{c} PbO + C \longrightarrow Pb + CO \\ PbO + CO \longrightarrow Pb + CO_{2} \\ CaO + SiO_{2} \longrightarrow CaSiO_{3} \ (slag) \\ PbSiO_{3} + CaO \longrightarrow PbO + CaSiO_{3} \\ (if \ formed) \end{array}$$

The slag and molten metal are drawn out from the furnace.

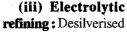
(iii) Purification: The lead obtained by any of the above two processes contains Bi, Sb, Cu, Fe, Ag, etc., as impurities.

The removal of these impurities is done by the following processes:

(i) Softening process: This process removes the base metals. The impure metal is melted on the shallow hearth of the reverberatory furnace and a current of air is circulated. The base metals are oxidised and come on the surface of the molten mass as scum which

(ii) Desilverisation: The removal of silver is done by Parke's process or Pattinson's process.

removed.



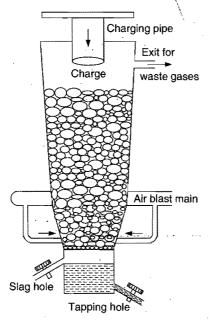


Fig. 9.11 Blast furnace

lead is further purified by Bett's electrolytic method. It consists of impure lead as anode and pure lead as cathode while lead silico fluoride,  $PbSiF_6$ , acts as an electrolyte. This contains 8 to 12% hydrofluosilicic acid  $(H_2SiF_6)$  and a little gelatin.

On passing current, pure lead is deposited on the cathode, the less electropositive impurities like Ag, Au, Sb, etc., collect below anode as anodic mud while more electropositive impurities like Fe, Zn, Ni, etc., go into the solution.

**Properties:** (i) It is a bluish grey metal. It has bright metallic lustre when freshly cut. It is soft in nature and can be cut with knife. It is a heavy metal (sp. gr. 11.35). It melts at 327°C.

- (ii) It leaves a black mark on paper.
- (iii) It is malleable but not ductile.
- (iv) It is poor conductor of electricity.
- (v) It is not attacked by dry air but affected by moist air with the formation of a thin film of basic carbonate on its surface which prevents the further action.
- (vi) When heated in air or oxygen, it forms lead monoxide which changes to red lead.

$$2Pb + O_2 \xrightarrow{\text{Heat}} 2PbO$$
 (Litharge)  
 $6PbO + O_2 \xrightarrow{\text{High temp}} 2Pb_3O_4$  (Red lead)

(vii) It is not affected by pure water except at the boiling point. It dissolves slowly in water containing dissolved oxygen.

$$2Pb + 2H_2O + O_2 \longrightarrow 2Pb(OH)_2$$

The dissolution of lead in water is known as plumbosolvency. The value of plumbosolvency increases if the water contains nitrates, organic acids and ammonium salts. The presence of soluble sulphates, phosphates, carbonates, etc., decrease the dissolution of lead due to formation of a protective thin layer of insoluble lead salts. Lead pipes are often used for conveying drinking water. In order to minimise the dissolution of lead in the form of lead salts which are poisonous, hard water is first passed through lead pipes as to deposit the protective film on the inner surface of the pipes.

(viii) Reaction with acids: Dilute HCl and  $H_2SO_4$  have practically no action on lead. Lead dissolves in hot conc. HCl with evolution of hydrogen.

$$3[Pb + 2HNO_3(dil.) \longrightarrow 2Pb(NO_3)_2 + 2H]$$

$$2[HNO_3 + 3H \longrightarrow NO + 2H_2O]$$

$$3Pb + 8HNO_3(dil.) \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

$$Pb + 2HNO_3(conc.) \longrightarrow Pb(NO_3)_2 + 2H$$

$$2[HNO_3 + H \longrightarrow NO_2 + H_2O]$$

$$Pb + 4HNO_3(conc.) \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$$
Organic acids dissolve lead in presence of oxygen.

$$Pb + 2CH_3COOH + \frac{1}{2}O_2 \longrightarrow Pb(CH_3COO)_2 + H_2O$$

Hot conc. H<sub>2</sub>SO<sub>4</sub> dissolves lead with evolution of SO<sub>2</sub> but the reaction becomes slower due to formation of insoluble PbSO<sub>4</sub>.

$$Pb + 2H_2SO_4 \longrightarrow PbSO_4 + SO_2 + 2H_2O$$

HNO<sub>3</sub> is the best solvent for lead. With dil. HNO<sub>3</sub>, NO is evolved while with conc. HNO<sub>3</sub>, NO<sub>2</sub> is liberated.

(ix) Reaction with NaOH: Lead dissolves in NaOH forming sodium plumbite with evolution of hydrogen.

$$Pb + 2NaOH \longrightarrow Na_2PbO_2 + H_2$$

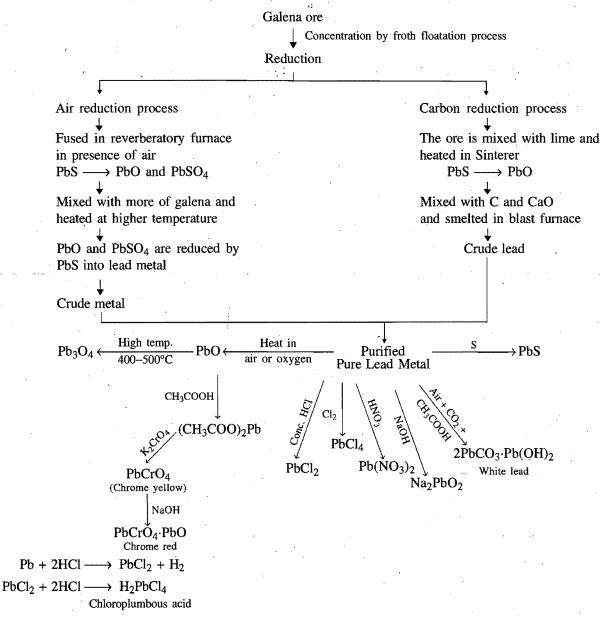
(x) Reaction with non-metals: Lead directly combines with sulphur and halogens.

$$Pb + S \longrightarrow PbS$$
  
 $Pb + 2Cl_2 \longrightarrow PbCl_4$ 

**Uses:** Lead is used:

- (i) for making chambers used in the manufacture of H<sub>2</sub>SO<sub>4</sub>.
- (ii) for making pipes for carrying water.
- (iii) for making telegraph and telephone wires which are to be buried in earth.
  - (iv) in making bullets and lead accumulators.
  - (v) in the preparation of lead pigments.
- (vi) in making useful alloys such as solder, type metal, pewter, etc.

### FLOW SHEET FOR THE EXTRACTION OF LEAD AND FORMATION OF VARIOUS COMPOUNDS



## 9.1 COMPOUNDS OF LEAD

#### 1. Lead Monoxide, PbO

It is known in two forms:

(i) a yellow powder commonly known as massicot and

(ii) a buff coloured crystalline form known as litharge.

**Preparation:** It is obtained by heating lead or lead sulphide in air at 300°C (massicot form). When the temperature of oxidation kept 900, litharge is formed.

$$2Pb + O_2 \longrightarrow 2PbO$$
  
 $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$ 

It is also formed by heating lead nitrate or lead carbonate.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$
  
 $PbCO_3 \longrightarrow PbO + CO_2$ 

**Properties:** It is insoluble in water. It is an amphoteric oxide. It dissolves in acids and alkalies both.

$$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$$

$$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$$

On heating in air at 470°C, it forms red lead.

$$6PbO + O_2 \longrightarrow 2Pb_3O_4$$
 (red lead)

**Uses:** It is used for making glass, paints and varnishes. The mixture of massicot and glycerine is used as a cement for glass and pottery. PbO is used for making other lead compounds.

## 2. Red Lead (Minium or Sindhur), Pb<sub>3</sub>O<sub>4</sub>

**Preparation:** It is obtained by heating litharge at 470°C in air.

$$6PbO + O_2 \xrightarrow{470^{\circ}C} 2Pb_3O_4$$

**Properties:** It is a red powder, insoluble in water. When heated, it becomes almost black but it again becomes red on cooling. On heating above 470°C, it decomposes into PbO and  $O_2$ .

$$2Pb_3O_4 \longrightarrow 6PbO + O_2$$

When treated with conc. HNO3, lead nitrate and brownish black insoluble oxide, PbO<sub>2</sub>, are formed. This indicates that Pb<sub>3</sub>O<sub>4</sub> is a compound oxide containing both PbO<sub>2</sub> and PbO in the ratio of 1:2.

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$
  
With  $H_2SO_4$ , it evolves oxygen.

$$2Pb_3O_4 + 6H_2SO_4 \longrightarrow 6PbSO_4 + 6H_2O + O_2$$

It acts as an oxidising agent.

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$$
  
 $Pb_3O_4 + 4C \longrightarrow 3Pb + 4CO$   
 $Pb_3O_4 + 4CO \longrightarrow 3Pb + 4CO_2$ 

Uses: It is used:

- (i) as a red pigment.
- (ii) in glass industry.
- (iii) for making protective paint for iron and steel.
- (iv) in match industry as an oxidising agent.

## 3. Lead Acetate (Sugar of Lead), (CH<sub>3</sub>COO)<sub>2</sub>Pb

Preparation: It is prepared by dissolving lead oxide (litharge) or lead carbonate or basic lead carbonate in acetic acid (45%) and crystallising the solution.

PbO + 2CH<sub>3</sub>COOH 
$$\longrightarrow$$
 (CH<sub>3</sub>COO)<sub>2</sub>Pb + H<sub>2</sub>O  
PbCO<sub>3</sub> + 2CH<sub>3</sub>COOH  $\longrightarrow$  (CH<sub>3</sub>COO)<sub>2</sub>Pb + CO<sub>2</sub> + H<sub>2</sub>O  
2PbCO<sub>3</sub> Pb(OH)<sub>2</sub> + 6CH<sub>3</sub>COOH  $\longrightarrow$   
3(CH<sub>3</sub>COO)<sub>2</sub>Pb + 2CO<sub>2</sub> + 4H<sub>2</sub>O

**Properties:** (i) It is a white crystalline solid. It is soluble in water. Its solution has sweet taste and known as sugar of lead but it is poisonous in nature.

(ii) On heating, it decomposes to give acetone.

$$(CH_3COO)_2Pb \longrightarrow PbO + CO_2 + CH_3COCH_3$$
Acetone

(iii) It forms a white precipitate of lead carbonate when treated with sodium bicarbonate.

$$(CH_3COO)_2 \cdot Pb + 2NaHCO_3 \longrightarrow PbCO_3 + 2CH_3COONa + CO_2 + H_2O$$

(iv) It forms a white precipitate of basic lead carbonate when treated with a solution of sodium carbonate.

$$3(CH_3COO)_2Pb + 3Na_2CO_3 + H_2O \longrightarrow$$
  
 $2PbCO_3 \cdot Pb(OH)_2 + 6CH_3COONa + CO_2$   
Basic lead carbonate

(v) A black precipitate is obtained when H<sub>2</sub>S is passed through its solution.

$$(CH_3COO)_2Pb + H_2S \longrightarrow PbS + 2CH_3COOH$$
  
Lead sulphide
(black)

(vi) A yellow precipitate of lead chromate is formed when potassium chromate solution is added.

$$(CH_3COO)_2Pb + K_2CrO_4 \longrightarrow PbCrO_4 + 2CH_3COOK$$

(vii) On addition of dil. HCl to a cold solution of lead acetate, a white precipitate of lead chloride appears. This precipitate is soluble in hot water.

$$(CH_3COO)_2Pb + 2HC1 \longrightarrow PbCl_2 + 2CH_3COOH$$

(viii) The solution of lead acetate on boiling with litharge (PbO) forms basic lead acetate.

$$(CH_3COO)_2Pb + PbO + H_2O \longrightarrow Pb(OH)_2Pb(CH_3COO)_2$$

Basic lead acetate.

**Uses:** It is used:

- (i) in the manufacture of chrome yellow and chrome red employed as lead pigments.
  - (ii) as a mordant in dyeing and calicoprinting.
  - (iii) for the manufacture of white lead.
- (iv) as a laboratory reagent for the test of sulphide and chloride ions.
  - (v) in medicine for curing skin diseases.

## 4. Basic Lead Carbonate (White Lead) 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub>

White lead is manufactured by the application of the following three methods:

- (i) Dutch process, (ii) Carter's process, (iii) Electrolytic process.
- 1. Dutch process: This is the oldest method but it produces the best quality of white lead. It is a very slow method and takes about 6 to 8 weeks for the conversion of lead metal into white lead in the presence of acetic acid, carbon dioxide and moist air.

Lead is melted and cast into the form of perforated discs, called buckles. A number of earthenware pots with shelves are taken in which vinegar or dilute acetic acid (3%) is placed at their bottom. Buckles are kept at the shelves of these earthenware pots. These pots are then arranged in rows. These are partly covered with wooden planks and the space in between the rows is fled by spent tanbark and horse dung (Fig. 9.12).

The pots are allowed to remain in this position for about 6 to 8 weeks. During this period, fermentation of tanbark and horse dung occurs. This produces CO2 and heat energy which helps in the evaporation of acetic acid. The combined action of acetic acid vapours, carbon dioxide, air and moisture converts lead into white lead. The following chemical changes are supposed to take place.

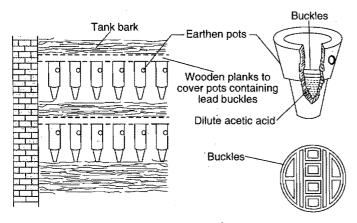


Fig. 9.12 Dutch process

$$\begin{aligned} & 2\text{Pb} + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 2\text{Pb}(\text{OH})_2 \\ & \text{Pb}(\text{OH})_2 + 2\text{CH}_3\text{COOH} \longrightarrow \text{Pb}(\text{CH}_3\text{COO})_2 + 2\text{H}_2\text{O} \\ & \text{Pb}(\text{OH})_2 + \text{Pb}(\text{CH}_3\text{COO})_2 \longrightarrow \text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{Pb}(\text{OH})_2 \\ & \text{Basic lead acetate} \\ & 3[\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{Pb}(\text{OH})_2] + 4\text{CO}_2 + 2\text{H}_2\text{O} \longrightarrow \end{aligned}$$

. 
$$2[2PbCO_3 \cdot Pb(OH)_2] + 6CH_3COOH$$
  
White lead

White lead is removed from unchanged lead and washed with water to remove soluble lead acetate. It is then dried.

**2.** Carter's process: It is comparatively quicker process. This process is carried in wooden cylinders which are rotated.

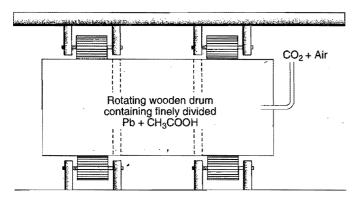


Fig. 9.13 Carter's process

Molten lead is first atomised by a jet of superheated steam or compressed air and brought in the wooden cylinders. A spray of acetic acid, carbon dioxide and air is blown into the cylinders (Fig. 9.13).

The same chemical changes occur as in the Dutch process. The conversion takes place in 5–12 days.

**3. Electrolytic process:** The electrolytic cell is divided into two compartments with the help of a porous diaphragm. The anodic compartment is filled with sodium acetate solution and contains anodes of lead plates, while cathodic compartment consists of cathodes of steel dipped into a solution of sodium carbonate. On passing electricity, lead of anode starts dissolving in the form of lead acetate, which meets with sodium carbonate to form white lead.

$$CH_{3}COONa \Longrightarrow CH_{3}COO^{-} + Na^{+}$$

$$Anode$$

$$dissolves lead$$

$$Pb(CH_{3}COO)_{2}$$

$$3Pb(CH_{3}COO)_{2} + 4Na_{2}CO_{3} + 2H_{2}O \longrightarrow$$

$$2PbCO_{3} \cdot Pb(OH)_{2} + 2NaHCO_{3} + 6CH_{3}COONa$$

White lead is washed with water and dried.

**Properties:** It is white, heavy amorphous powder. It is insoluble in water. It is poisonous in nature. It is miscible with linseed oil. On heating to 430°C, it decomposes into red lead.

$$\begin{array}{c} \text{2PbCO}_3 \cdot \text{Pb(OH)}_2 \longrightarrow \begin{array}{c} \text{Pb}_3 \text{O}_4 + \text{H}_2 \text{O} + \text{CO} + \text{CO}_2 \\ \text{Red lead} \end{array}$$

It is darkened in air due to formation of PbS.

**Uses:** White lead mixed with linseed oil is used as a white paint. It has a large covering power. It is generally mixed with BaSO<sub>4</sub> which increases its property of brushing out without affecting its covering power.

The main drawbacks to the use of white lead are that it becomes black if H<sub>2</sub>S is present in atmosphere and it is poisonous in nature. Various substitutes such as lithopone, titanium dioxide, sublimed white lead, etc., have been suggested. It is also used for the preparation of red lead and pottery glazes.

## SOME SOLVED PROBLEMS

**Example 1.** A colourless solution contains a metal nitrate. A little solution of sodium chloride is added to it when a cloudy white precipitate appears. How you will ascertain about the metal ion?

#### **Solution:**

The chloride ions have combined with the metal ions to give the precipitate of a chloride as sodium nitrate is soluble.

Metal nitrate + NaCl 
$$\longrightarrow$$
 Metal chloride + NaNO<sub>3</sub> (Insoluble) (Soluble)

The metal chloride may be PbCl<sub>2</sub> or AgCl or Hg<sub>2</sub>Cl<sub>2</sub>. The following tests can be used to ascertain the metal chloride.

- (i) If the precipitate dissolves in hot water, it is PbCl<sub>2</sub>.
- (ii) If the precipitate dissolves in NH<sub>4</sub>OH, it is AgCl.
- (iii) If the precipitate turns black with NH<sub>4</sub>OH, it is Hg<sub>2</sub>Cl<sub>2</sub>.

**Example 2.** (a) If you have to dissolve lead (II) oxide, PbO, which acid you will choose?

(b) Explain why the reactions with hydrochloric acid and sulphur dioxide show the oxidising nature of  $PbO_2$ .

(c) Predict the result of reacting Pb<sub>3</sub>O<sub>4</sub> with concentrated hydrochloric acid. [M.L.N.R. 1992]

#### **Solution:**

(a) Nitric acid. This is because lead nitrate formed is soluble in water. If H<sub>2</sub>SO<sub>4</sub> is used, an insoluble layer of PbSO<sub>4</sub> is deposited on the surface of powder and prevents the further reaction. Likewise, PbCl<sub>2</sub> prevents the reaction with HCl.

$$\begin{array}{ccc} & \text{IV} & \text{II} \\ & \text{PbO}_2 + 4\text{HCI} \longrightarrow & \text{PbCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O} \\ & \text{IV} & \text{II} \\ & \text{PbO}_2 + \text{SO}_2 & \longrightarrow & \text{PbSO}_4 \end{array}$$

In above reactions, lead changes from lead (IV) to lead (II), *i.e.*, gain of electrons.

$$Pb^{4+} + 2e \longrightarrow Pb^{2+}$$

Thus, PbO<sub>2</sub> acts as oxidising agent as it oxidises HCl and SO<sub>2</sub>

(c) Pb<sub>3</sub>O<sub>4</sub> is considered to possess PbO and PbO<sub>2</sub>· PbO<sub>2</sub> acts as an oxidising agent. Thus, PbCl<sub>2</sub> and Cl<sub>2</sub> are formed.

$$Pb_{3}O_{4} \longrightarrow 3PbO + O$$

$$2HCl + O \longrightarrow H_{2}O + Cl_{2}$$

$$[PbO + 2HCl \longrightarrow PbCl_{2} + H_{2}O] \times 3$$

$$Pb_{3}O_{4} + 8HCl \longrightarrow 3PbCl_{2} + Cl_{2} + 4H_{2}O$$

## **Example 3.** Explain the following:

- (i) The first ionisation energy of carbon atom is greater than that of boron atom whereas the reverse is true for second ionisation energy.
  - (ii)  $(SiH_3)_3N$  is a weaker base than  $(CH_3)_3N$ . [I.I.T. 1995]
  - (iii) Diamond is very hard while graphite is soft.

[I.I.T. 1993]

- (iv)  $CO_2$  is a gas while silica is a solid.
- (v) Solid carbon dioxide is known as dry ice.

#### **Solution:**

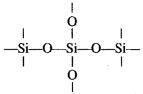
(i) The first ionisation energy of carbon  $(1s^2, 2s^2 2p_x^{-1}2p_y^{-1})$  is higher than boron  $(1s^2, 2s^22p_x^{-1})$  as the nuclear charge in carbon is higher than boron (At. no. C = 6; B = 5).

The second ionisation energy of carbon is less than that of boron because in carbon the second electron is to remove from 2p-orbital while in boron the second electron is to be removed from paired 2s-orbital which requires higher energy in comparison to singly occupied p-orbital.

- (ii) In  $(SiH_3)_3 N$ , the lone pair of electrons on nitrogen is involved in  $p\pi$ — $d\pi$  back bonding, while such bonding is not possible in  $(CH_3)_3 N$ , as d-orbitals are not present in carbon. Hence, the lone pair of electrons on nitrogen in  $(CH_3)_3 N$  is available for donation to Lewis acids, thereby acting as stronger base.
- (iii) Diamond has giant three dimensional polymeric structure in which each carbon is  $sp^3$  hybridized and linked to four carbon atoms. This structure makes diamond as hardest. On

account of small radii of carbon atoms, the various atoms are closely packed in the crystal lattice. Graphite possesses layer structure in which each carbon atom is  $sp^2$  hybridized. There is wide separation between various layers. One layer can slide easily on the other. This makes graphite soft in nature.

(iv) In carbon dioxide discrete molecules are present. In each molecule carbon is linked with two oxygen atoms by double bonds (O=C=O), while silica possesses a giant three dimensional structure in which each silicon is linked with four oxygen atoms tetrahedrally and each oxygen is linked with two silicon atoms.



This structure is extremely stable and considerable energyis required to break Si—O bond. Thus, CO<sub>2</sub> is a gas and silica is a solid.

(v) When solid  $CO_2$  evaporates, it changes to the gaseous state without coming to the liquid state. It produces cooling during evaporation. It is, therefore, known as dry ice.

**Example 4.** Write the formulae of the following compounds:

(a) Butter of tin

(b) White lead

(c) Red lead

(d) Sugar of lead

(e) Litharge

(f) Carborundum

(g) Phosgene

(h) Chrome yellow

(i) Water glass

(j) Drykold

#### **Solution:**

(a) SnCl<sub>4</sub>·5H<sub>2</sub>O

(Stannic chloride)

(b) 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub>

(Basic lead carbonate)

(c) Pb<sub>3</sub>O<sub>4</sub>

(Trilead tetra-oxide)

(d) Pb(CH<sub>3</sub>COO)<sub>2</sub>

(Lead acetate)

(e) PbO

(Lead monoxide)

(f) SiC

(Silicon carbide)

(g) COCl<sub>2</sub>

(Carbonyl chloride)

(h). PbCrO<sub>4</sub>

Tand alamanaka)

(11): 1 - - - - - 4

(Lead chromate)

(i) Na<sub>2</sub>SiO<sub>3</sub>

(Sodium silicate)

(j) CO<sub>2</sub>

(Carbon dioxide in solid state)

**Example 5.** An aqueous solution of a salt (A) gives a white precipitate (B) with sodium chloride solution. The filtrate gives a black precipitate (C) when  $H_2S$  is passed into it. Compound (B) dissolves in hot water and the solution gives a yellow precipitate (D) on treatment with sodium iodide. The compound (A) does not give any gas with dilute HCl but liberates a reddish brown gas on heating. Identify the compounds (A) to (D).

#### **Solution:**

Since the crystalline compound (B) dissolves in hot water

and gives a yellow precipitate with NaI, it should be lead chloride, PbCl<sub>2</sub> and the solution (A) consists a lead salt.

$$PbCl_2 + 2NaI \longrightarrow PbI_2 + 2NaCl$$
<sub>(B)</sub>
<sub>(D)</sub>

The compound (A) does not give any gas with dilute HCl but liberates a reddish brown gas on heating, it should be lead nitrate,  $Pb(NO_3)_2$ .

$$\begin{array}{ccc} 2Pb(NO_3)_2 & \longrightarrow & 2PbO + 2NO_2 + O_2 \\ (A) & & \text{Reddish brown gas} \end{array}$$

Lead chloride is sparingly soluble in water. When H<sub>2</sub>S is passed, it gives a black precipitate of lead sulphide, PbS.

$$PbCl_2 + H_2S \longrightarrow PbS + 2HCl$$
Black
(C)

Thus,

- (A) is lead nitrate,  $Pb(NO_3)_2$ ,
- (B) is lead chloride, PbCl<sub>2</sub>,
- (C) is lead sulphide, PbS,

and

(D) is lead iodide, PbI<sub>2</sub>.

**Example 6.** (i) Indicate the principal ingredients of the following:

- (a) Coal gas (b) Producer gas (c) Water gas. [M.L.N.R.1991]
- (ii) Identify A and B (compound/reaction condition):

$$PbS \xrightarrow{Heat} A + PbS \xrightarrow{B} Pb + SO_2$$
 [1.1.T. 1991]

#### Solution:

- (i) Coal gas,  $H_2 + CH_4 + CO$ Producer gas,  $CO + N_2$ Water gas,  $CO + H_2$
- (ii) A = PbO or  $\text{PbSO}_4$  B = high temperatureAir supply is cut off.

**Example 7.** Write the balanced equation for reaction of  $Al_4C_3$  and CaNCN with water. [I.I.T. 2002]

#### **Solution:**

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$
.  
 $CaNCN + 3H_2O \longrightarrow CaCO_3 + 2NH_3$ .

**Example 8.** Like CO why its analogue SiO is not stable? [C.B.S.E. (P.M.T.) 2004]

#### **Solution:**

Carbon has a strong tendency to form  $p\pi-p\pi$  multiple bonds due to its small size and high electronegativity. Carbon combines with oxygen and forms stable CO forming  $p\pi-p\pi$  multiple bonds. CO is actually a resonance hybrid of the following two structures:

$$:C = 0: \longleftrightarrow :C = 0:$$

Silicon, on the other hand, on account of its bigger size and lower electronegativity has no tendency to form  $p\pi-p\pi$  multiple bonds and thus does not combine with oxygen to form stable SiO.

**Example 9.**  $[SiF_6]^{2-}$  is known whereas  $[SiCl_6]^{2-}$  not. Give possible reasons.

#### **Solution:**

The possible reasons for the non-existence of  $[SiCl_6]^{2-}$  are:

- (i) due to large size of Cl atoms. Six fluorine atoms can be easily accommodated around silicon atom due to smaller size while six larger chlorine atoms cannot be accommodated around silicon atom.
- (ii) due to the presence of lone pair of electrons in fluorine atom on a smaller 2p-orbital, the interaction with d-orbital of silicon atom is stronger rather than the presence of lone pair of electrons in chlorine atom on a larger 2p-orbital, the interaction with d-orbital of silicon atom is poor.

**Example 10.** (a) Why Sn(II) is a reducing agent whereas Pb(II) is not?

- (b) Why does not silicon form an analogue of graphite?
- (c) C and Si are always tetravalent but Ge, Sn and Pb show divalency. Why?

#### **Solution:**

(a) Both Sn and Pb exhibit +2 and +4 oxidation states due to inert pair effect. Inert pair effect is more effective in lead than in tin. Thus, +2 state is less stable in tin and thus, Sn(II) acts as a reducing agent and converted into more stable Sn(IV) state. For example, Fe<sup>3+</sup> is reduced by Sn(II).

$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

- (b) On account of bigger size and smaller electronegativity of silicon atom in comparison to carbon atom, silicon atom does not undergo  $sp^2$ -hybridization and does not form  $p\pi$ - $p\pi$  double bonds. Thus, silicon does not form graphite like structure as it requires double bonds:
- (c) Carbon and silicon have no d- or f-electrons in inner shells. Therefore, they do not show inert pair effect. Consequently, they show only tetravalency due to  $sp^3$  hybridization. In all other elements from Ge to Pb either d- or both d- and f-electrons are present. Due to poor shielding effect, inert pair effect is observed, i.e., showing either divalency or tetravalency. The stability of divalency increases while that of tetravalency decreases as the inert pair effect becomes more and more prominent from Ge to Pb.

**Example 11.** (a) Silica is attacked by hydrofluoric acid with the formation of  $SiF_6^{2-}$  anions. The analogous  $CF_6^{2-}$  anion does not exist. Account for this.

(b) Diamond is covalent, yet it has a high melting point. Why? **Solution:** 

(a) Silicon has 3d-orbitals in the valence shell and thus expands its octet giving  $sp^3d^2$ -hybridization while d-orbitals are not present in the valence shell of carbon. It can undergo  $sp^3$ -hybridization only. Thus, carbon is unable to form  $CF_6^{2-}$  anion.

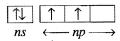
- (b) Diamond has three dimensional network involving strong C—C bonds which are difficult to break. Hence, its a high melting point.
- **Example 12.** (a) Discuss briefly why tin and lead compounds do not show  $p\pi$ - $p\pi$  bonding?
- (b) What are the properties responsible for the anomalous behaviour of carbon?
  - (c) Which silicon compound is used as a:
  - (i) dehydrating agent
- (ii) cation exchanger
- (iii) lubricant
- (iv) thermal insulator.

#### **Solution:**

- (a) Tin and lead do not show  $p\pi-p\pi$  bonding because the *d*-orbitals of Sn and Pb are of much higher energy than that of the element with which they form a bond in the compound.
- (b) Small size, high electronegativity, high ionisation energy and absence of *d*-orbitals in the valence shell are the main properties of carbon which lead to its anomalous behaviour.
  - (c) (i) Silica gel
- (ii) Zeolites
- (iii) Silicones
- (iv) Asbestos

## SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Group IVA or 14 of the periodic table consists of six elements—carbon, silicon, germanium, tin, lead and ununquadium. These are p-block elements as the last differentiating electron is accommodated in np-shell. These elements have four electrons in their valency shell, two of which are in s-orbital while remaining two in p-orbitals, i.e., ns<sup>2</sup>np<sup>2</sup> configuration.



- 2. Carbon is seventeenth and silicon is second most abundant element by mass in earth's crust. Carbon is found both in native and combined state. Carbon is an essential constituent of all living matter as proteins, carbohydrates and fats. Silicon occurs very widely as silica and a wide variety of silicate minerals and clays. Tin and lead are comparatively low but are found as concentrated ores. The important ore of tin is cassiterite (SnO<sub>2</sub>) and that of lead is galena (PbS). Germanium is rare element.
- 3. (a) Non-metallic nature decreases from carbon to lead.

C Si

Ge Metalloid Sn Pb Metals

- (b) Density increases from C to Pb.
- (c) Melting and boiling points decrease down the group.
- (d) Atomic radii increase on moving down the group.
- (e) Electronegativity decreases from C to Si.
- (f) Ionisation energy decreases regularly from C to Sn. Pb, however, shows a higher value than Sn due to poor shielding of *f*-orbitals.
- **4.** All the elements show tetravalency due to  $sp^3$  hybridization. Last three members show inert pair effect and show the tendency to form  $M^{2+}$  ions. The stability of  $M^{2+}$  state increases as the atomic number increases. The compounds of  $Ge^{2+}$  and  $Sn^{2+}$  are less stable than  $M^{4+}$  state. Thus,  $Ge^{2+}$  and  $Sn^{2+}$  compounds act as **reducing agents**.

  Ph<sup>2+</sup> compounds are more stable than  $Ph^{4+}$  compounds
  - Pb<sup>2+</sup> compounds are more stable than Pb<sup>4+</sup> compounds. Thus, Pb<sup>4+</sup> compounds act as oxidising agents.
- 5. The tendency of formation of long open or closed chains by the combination of same atoms in themselves is known as catenation. This property is maximum in carbon and decreases down the group. Lead shows no catenation.

Only carbon atoms do form double or triple bonds involving  $p\pi$ – $p\pi$  bonding. Carbon has also the property to form closed chain compounds with O, S and N atoms as well as forming  $p\pi$ – $p\pi$  multiple bonds with other elements particularly N, S and O. Carbon can form chains containing as many as carbon atoms but Si and Ge cannot extend the chain beyond 6 atoms. The reason for greater tendency of carbon for catenation is due to high bond energy between carbon and carbon atoms. This bond energy is approximately of the same magnitude as the energies of the bond between carbon and atoms of other elements.

C-C (83 kcal mol<sup>-1</sup>); C-O (86 kcal mol<sup>-1</sup>);

C— $Cl(81 kcal mol^{-1})$ 

- **6.** The maximum covalency of carbon is four because it has no *d*-orbitals which can be used to accommodate more than 8 electrons.
  - Remaining elements have vacant d-orbitals. Thus, they have the tendency to show maximum covalency of six involving  $sp^3d^2$ -orbitals.
- 7. The phenomenon of existence of a chemical element to exist in two or more forms differing in physical properties but having almost same chemical nature is known as allotropy. This phenomenon is due to the difference either in the number of atoms in the molecules or arrangement of atoms in the molecules in the crystal structure. Except lead, all other members of group 14 exhibit allotropy.
  - Carbon exists as diamond, graphite, coal, charcoal, lampblack and fullerene. Silicon exists in two forms, crystalline and amorphous; germanium exists in two crystalline forms and tin exists in three forms; grey, white and rhombic form.
- **8.** Diamond is the purest form of carbon. It is the crystalline form. It is the hardest natural substance known. It is bad conductor of electricity and heat. It is transparent to X-rays and glows in ultraviolet rays. It has high refractive index (2.45). It is chemically inert. It reacts with fluorine at 700°C to form CF<sub>4</sub>. In diamond every carbon is in  $sp^3$  hybridized state and linked to four other carbon atoms tetrahedrally by covalent bonds. It is, thus, a giant three dimensional polymeric structure in which C—C distance is 1.54 Å and bond angle 109.5°. It is used as gem stone and in knifes for cutting glasses and rock borers.

- 9. Graphite is another crystalline form of carbon. It is found in nature and is also manufactured by Acheson process. It is soft, greasy, dark greyish coloured crystalline solid. It is good conductor of electricity. It leaves a black mark on paper and is called black lead or plumbago. It is chemically more active than diamond. With alkaline KMnO<sub>4</sub>, it is oxidised to mellitic acid [C<sub>6</sub>(COOH)<sub>6</sub>] and oxalic acid. Conc. HNO<sub>3</sub> or conc. H<sub>2</sub>SO<sub>4</sub> oxidises it into insoluble yellowish green substance, known as graphitic acid C<sub>11</sub>H<sub>4</sub>O<sub>5</sub>.
  - It has two dimensional sheet structure. Each carbon is  $sp^2$  hybridized and is linked to three carbon atoms in hexagonal planar structure. The C—C bond distance is 1.42 Å. The adjacent layers are held by van der Waals' forces and distance between layers is 3.4Å. Graphite is thermodynamically more stable form.
  - It is used for lining and making electrodes, refractory crucibles, lead pencils. It acts as a moderator in nuclear reactor. It is also used as a lubricant in machinery.
- 10. An allotropic form called fullerenes or Buckminster-fullerenes or Bucky balls recently discovered is C<sub>60</sub> or C<sub>70</sub>. Such molecules are made from interlocking hexagonal and pentagonal rings of carbon atoms and exist in chimney soot or candle smoke.
- 11. Carbon has three amorphous forms. These are coal, charcoal and lampblack. Coal is the crude form of carbon. It is found in various forms depending upon the carbon content (peat, lignite, bituminous, steam coal and anthracite). Anthracite is the superior quality of coal.
  - When coal is subjected to destructive distillation, it loses volatile constituents and the residue left is known as **coke**. Coal is used as a fuel, for making fuel gases and synthetic petrol and coke.
  - Charcoal is formed when wood, cellulose or any other carboneous matter are burnt in limited supply of air. This is the most active form. It has number of applications.
  - Lampblack, carbon black or soot is obtained by burning substances rich in carbon such as kerosene, turpentine oil, etc., in a limited supply of air. These substances yield a large amount of smoke which is passed into chambers having wet blankets. The soot collected on blankets is called lampblack. It is almost pure carbon. It is a soft black powder and is used as a pigment in black inks and paints. It is also used as a filler in making rubber tyres.
- 12. The elements of group 14 react with oxygen on strong heating to form oxides of the type  $MO_2$ . The acidic nature decreases with increase in atomic number.  $CO_2$  and  $SiO_2$  are acidic while  $GeO_2$ ,  $SnO_2$  and  $PbO_2$  are amphoteric in nature. They dissolve in alkalies forming carbonates, silicates, germanates, stannates and plumbates of the type  $Na_2MO_3$  respectively.
  - They also form oxides of the type MO.SiO is unstable. CO is neutral while SnO and PbO are amphoteric.
- 13. Non-oxidising acids do not attack carbon and silicon. Tin dissolves slowly in dilute HCl but readily in conc. HCl. Lead also dissolves in HCl forming insoluble PbCl<sub>2</sub>. Germanium is not attacked by dilute HCl but when metal is heated in a

- stream of HCl gas, germanium chloroform (GeHCl<sub>3</sub>) is formed. Concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> attack Ge, Sn and Pb.
- **14.** Except carbon, all other members of group 14 dissolve in aqueous NaOH solution evolved hydrogen.

$$M + 2$$
NaOH + H<sub>2</sub>O  $\longrightarrow$  Na<sub>2</sub> $M$ O<sub>3</sub> + 2H<sub>2</sub>

- **15.** All the members of group 14 form covalent hydrides of type  $MH_4$ . Besides  $CH_4$ , carbon forms a large number of hydrides, saturated and unsaturated. Silicon forms only limited number of saturated hydrides. Germanium gives a still smaller number while Sn and Pb form only one hydride each. Hydrides are gaseous and their thermal stability decreases and consequently reducing nature increases.
- **16.** All the members of group 14 form tetrahalides of the type  $MX_4$  except PbBr<sub>4</sub> and PbI<sub>4</sub>. The halides are covalent and formed by  $sp^3$  hybridization. The thermal stability decreases.

 $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$ Except carbon halides, other halides are readily hydrolysed by water. The hydrolysis is due to utilization of *d*-orbitals. The tetrahalides of Si, Ge, Sn and Pb can form hexahalo complexes. The tetrahalides of Si, Ge, Sn and Pb act as strong Lewis acids.

- 17. CO is a colourless, odourless, poisonous and neutral oxide. It is slightly soluble in water. It is obtained by heating K<sub>4</sub>Fe(CN)<sub>6</sub> with conc. H<sub>2</sub>SO<sub>4</sub>. It is absorbed by ammonical Cu<sub>2</sub>Cl<sub>2</sub> solution. It is combustible but does not support combustion. Its poisonous nature is due to its reaction with haemoglobin to form carboxy-haemoglobin which is not capable of absorbing oxygen. It is a good reducing agent. The bonding in CO is represented as: C ⊆ O. It acts as a π-acid ligand. It forms addition compound with a number of substances. It combines with metals like Ni, Cr, Fe, etc. The compounds formed are called carbonyls.
  - It is used as a fuel in the form of water gas, producer gas, etc. It is used in the manufacture of methanol, synthetic petrol, formic acid, phosgene gas, etc. It is used as a reducing agent in extraction of iron and in Mond's process for extraction of Ni.
- 18. CO<sub>2</sub> is a colourless, odourless and tasteless gas. It is present in atmosphere. It is slightly soluble in water but more soluble under pressure. It is heavier than air. It is easily liquefied under pressure into a colourless mobile liquid. If CO<sub>2</sub> under pressure is allowed to escape through a nozzle, a white solid, i.e., dry ice is obtained. Solid CO<sub>2</sub> is soft, white, snow like substance. It sublimes and leaves no residue. Solid CO<sub>2</sub> is used as a refrigerant under the commercial name drikold.

It is neither combustible nor a supporter of combustion. However, burning magnesium, sodium or potassium continues burning in the gas.  $CO_2$  is converted by plants into glucose and higher carbohydrates in the presence of sunlight and chlorophyll. This process is known as **photosynthesis**. **Carbogen** is a mixture of  $O_2$  and  $CO_2$  (5 to 10%). It is used for artificial respiration.

A mixture of solid  $CO_2$  and ether is used to produce low temperature of the order of  $-80^{\circ}$ C to  $-100^{\circ}$ C.  $CO_2$  is used as a fire extinguisher.

- (a) Dry powder extinguishers contain sand and baking soda (NaHCO<sub>3</sub>).
- (b) Baking soda and sulphuric acid type extinguishers.
- (c) Foamite extinguishers contain baking soda and aluminium sulphate.
- 19. The carbides are binary compounds in which carbon combines with elements of lower or about equal electronegativity. Carbides are divided into three categories.
  - (i) Salt-like or ionic or electrovalent carbides: These are formed by strong electropositive elements of group 1, 2 and 13 (except boron), coinage metals, Zn, Cd and some lanthanides. These are further classified into three classes:
    - (a) Methanides: These give methane on hydrolysis. They contain  $C^{4-}$  ions, e.g., Be<sub>2</sub>C, Al<sub>4</sub>C<sub>3</sub>.
    - (b) Acetylides: These give acetylene on hydrolysis. They contain  $C_2^{2-}(C \equiv C)^{2-}$  ions, e.g.,  $CaC_2$ ,  $BeC_2$ ,  $Li_2C_2$ ,  $Na_2C_2$ , etc.
    - (c) Allylides: These give propyne or allylene on hydrolysis. These contain  $C_3^4$  ion, e.g.,  $Mg_2C_3$ .
  - (ii) Covalent carbides: Boron carbide and carborundum (SiC) belong to this category. They are covalent, polymeric, thermally stable, extremely hard, high melting and inert solids. SiC has diamond like structure.
  - (iii) Metallic or interstitial carbides: These are formed by transitional elements. Carbon atoms being small in size occupy interstitial positions of metal atoms. These carbides are hard and possess high melting points, used as refractory materials.
- **20.** Water gas, producer gas, coal gas, oil gas, natural gas, LPG, etc., are gaseous fuels. These have high calorific values.
  - (i) Water gas or synthetic gas is a mixture of CO and H<sub>2</sub>. It is made by passing steam over red hot coal at 1000 − 1400°C.
  - (ii) Producer gas is a mixture of CO and N<sub>2</sub>. It is made by passing air on hot coke. It has lower calorific value than water gas.
  - (iii) Coal gas is a mixture of hydrogen, methane, carbon monoxide, acetylene, etc. It is obtained by destructive distillation of coal at 1000°C. It has high calorific value.
  - (iv) Oil gas is obtained by cracking of kerosene. It is a mixture of lower hydrocarbons.
  - (v) Natural gas mainly contains CH<sub>4</sub>.
  - (vi) LPG is a mixture of butane and isobutane.
  - (vii) Semiwater gas is a mixture of water gas and producer gas.
- 21. Silicon is the second most abundant element in the earth's crust (about 28% by mass). Unlike carbon, it is never found in free state but always in combined state. Silicon is widely present as silica (SiO<sub>2</sub>) in various forms such as sand, quartz, flint, etc. Silicon exists in two forms (a) amorphous and (b) crystalline. The amorphous variety is obtained by heating dry powdered silica with magnesium. The crystalline form is obtained by heating finely powdered sand or quartz with carbon in an electric furnace.

- Amorphous silicon is chemically more active than crystalline silicon.
- 22. Sodium silicate is commercially called water glass. It is chemically sodium metasilicate containing an excess of silica. Its composition varies from Na<sub>2</sub>SiO<sub>3</sub>·SiO<sub>2</sub> to Na<sub>2</sub>SiO<sub>3</sub>·3SiO<sub>2</sub>. It is soluble in water and its solution is alkaline. Some coloured salts like cobalt nitrate, nickel chloride, ferrous sulphate, copper sulphate, etc., are placed in the solution of sodium silicate and whole solution is left as such for a night. A beautiful hollow tubes of metallic silicate gels possessing colours shoot up from these crystals and look like plants. This is called **silica garden**.
- 23. Silicones are organosilicon polymers containing Si—O—Si linkages. These are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerization. The substituted chlorosilanes are formed by the reaction of Grignard reagents and silicon tetrachloride.

 $RMgCl + SiCl_4 \longrightarrow R \longrightarrow SiCl_3$  or  $R_2SiCl_2$  or  $R_3SiCl$ .  $R_2SiCl_2 \stackrel{HOH}{\longrightarrow} R_2Si(OH)_2 \longrightarrow HO \longrightarrow Si(R_2) \longrightarrow O\longrightarrow Si(R_2) \longrightarrow OH$ Polymerization continues on both ends and thus chain increases in length (linear thermoplastic polymer)  $RSiCl_3 \stackrel{HOH}{\longrightarrow} RSi(OH)_3$ . This gives crossed linear silicone. Lower silicones are oily liquids while higher members containing long chains or ring structures are waxy and rubber like solids. These are stable towards heat and chemical reagents and are good electrical insulators. These are nontoxic and are water repellents. These have variety of industrial applications.

- **24.** Silicates are metal derivatives of silicic acid, H<sub>4</sub>SiO<sub>4</sub> or Si(OH)<sub>4</sub>. Silicates are formed by heating metal oxides or carbonates with sand. Silicates have basic unit SiO<sub>4</sub><sup>4</sup>. Each silicon atom is tetrahedrally bonded to four oxide ions.
  - (i) Orthosilicates Contain single discrete unit of SiO<sub>4</sub><sup>4</sup>-tetrahedra, e.g., zircon (ZrSiO<sub>4</sub>).
  - (ii) Pyrosilicates Contain two units of SiO<sub>4</sub><sup>4</sup> joined along a corner containing oxygen. Pyrosilicate ion, Si<sub>2</sub>O<sub>7</sub><sup>6</sup>, e.g., thorteveitite Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>.
  - (iii) Cyclic or ring silicates General formula  $(SiO_3^2)_n$ , e.g., beryl Be<sub>3</sub>Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>.
  - (iv) Chain silicates By sharing two oxygen atoms of each tetrahedra.
  - (v) Two dimensional sheet silicates By sharing three oxygen atoms of each tetrahedra. General formula  $(Si_2O_5)_n^{2n-}$ .
  - (vi) Three dimensional sheet silicates Involve all the four oxygen atoms of each tetrahedra examples quartz, tridymite, feldspar, ultramarines, etc.
- 25. Glass is a transparent or translucent super cooled solid solution of silicates and borates. The most common silicates are those of sodium, potassium, calcium and lead. An approximate formula is R<sub>2</sub>O<sub>2</sub>MO<sub>2</sub>6SiO<sub>2</sub>, where R = Na or K and M = Ca, Ba, Zn or Pb. SiO<sub>2</sub> may be replaced by Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>.
- **26.** Glass is attacked by HF. This property is used in the etching of glass.

- 27. The most important ore of tin is cassiterite, SnO<sub>2</sub>. The ore is crushed and powdered. It is washed with running water to remove lighter siliceous matter. Iron tungstate is removed by electromagnetic separator. The ore is now roasted to remove sulphur and arsenic. The roasted mass is mixed with about one fifth of its mass with anthracite (carbon) and subjected to heat in a reverberatory furnace. The liquid metal is drawn off from the furnace. It is further purified by liquation and poling.
- **28.** (a) Tin produces a peculiar sound whenever it is bent. The cracking sound is known as **Tincry.** 
  - (b) It exists in three allotropic forms. White tin is the common and most stable.

Grey tin 
$$\frac{18^{\circ}\text{C}_{\searrow}}{\checkmark}$$
 White  $\frac{170^{\circ}\text{C}}{\checkmark}$  Rhombic

The conversion of white tin to grey tin in cold countries is accompanied by decrease in density, comes into powdered form. This is termed **tin disease** or **tin pest** or **tin plague**.

- (c) Tin is not attacked by organic acids. This property is utilised for tinning cooking vessels made of copper or brass.
- (d) Tin is largely used in forming a protective coating over iron. The process of depositing tin over the sheets of iron or steel is called **tin plating.**
- (e) Tin foil is used for wrapping cigarettes, confectionary and for making the tooth-paste tubes. Tin amalgam is used in making mirrors.
- (f) It is used for making useful alloys.
  (i) Solder Sn 67%, Pb 33% (ii) Bronze Cu 75–90%,
  Sn 10 25% (iii) Bell metal Cu 80%, Sn 20%.
- 29. SnCl<sub>4</sub> is hygroscopic and forms crystalline hydrates containing 3, 5, 6 and 8 molecules of water as water of crystallization. The pentahydrate, SnCl<sub>4</sub>·5H<sub>2</sub>O is known as butter of tin or oxymuriate of tin. It is used as a mordant, for

- fire proofing cotton and for increasing weight of silk.
- 30. SnCl<sub>2</sub>·2H<sub>2</sub>O is a crystalline solid. It is soluble in water. It acts as a reducing agent. It is used for making **purple of cassius** and as a mordant.
- **31.** Lead is mainly extracted from galena (PbS) ore. The ore is concentrated by froth floatation process. It is extracted either by air reduction process or carbon reduction process.
- 32. Pb is not affected by pure water. However, it dissolves slowly in water having dissolved oxygen. The dissolution of lead in water is known as **plumbosolvency**. Lead salts are poisonous in nature and lead pipes are often used in conveying water. In order to minimise dissolution, hard water is first conveyed which forms a protective layer on the inner walls.
- 33. Lead forms three oxides PbO, PbO<sub>2</sub> and Pb<sub>3</sub>O<sub>4</sub>. PbO<sub>2</sub> is a strong oxidising agent. Pb<sub>3</sub>O<sub>4</sub> is known as red lead (minium or sindhur). PbO<sub>2</sub> is used in storage batteries and in match industry. PbO exists in two forms (a) a yellow powder commonly known as massicot and (b) buff coloured form known as litharge. PbO is used for making glass, paints and varnishes.
- **34.** The solution of lead acetate is sweet in taste and is known as sugar of lead but it is poisonous in nature.
- 35. Basic lead carbonate (white lead), 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> in linseed oil is used as white paint. It has large covering power but is poisonous and affected by H<sub>2</sub>S in air.
- 36. PbCrO<sub>4</sub>, chrome yellow is used as a yellow pigment and basic lead chromate PbCrO<sub>4</sub>·PbO known as chrome red, is also used as pigment.
- **37.** PbCl<sub>2</sub> is more ionic than PbCl<sub>4</sub>. It is more stable.
- **38.** Lead blocks are used to protect harmful emissions from radioactive minerals.
- **39.** Tetraethyl lead Pb(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> is used as an **antiknock** agent to improve the quality of gasoline.
- **40.** The hardness order of some abrasives is:
  Boron nitride > Diamond > Boron carbide > Silicon carbide

## Subjective Type Questions

#### 1. Answer the following:

- (a) Name three allotropic forms of carbon. Which one is a good conductor of electricity?
- (b) What is name of recently discovered allotrope of carbon, i.e., C<sub>60</sub>?
- (c) Which isotope of carbon is radioactive?
- (d) Which allotrope of carbon is used as a moderator in atomic reactors?
- (e) Name the purest form of carbon.

#### 2. Among group 14 elements name :

- (a) The element having highest tendency to form  $p\pi$ - $p\pi$  bonds.
- (b) The element which is most electropositive.
- (c) The element which is radioactive in nature.

- (d) The element which is most abundant in earth's crust.
- (e) The element which is used as a semiconductor.
- (f) The element which is commonly found in +2 oxidation state.

#### 3. Give reason for each of the following:

- (i) Why Ge, Sn and Pb show divalency?
- (ii) Out of methane and silane which is more stable and why?
- (iii) Aqueous solutions of carbonates of alkali metals are alkaline in nature?
- (iv) Carbon tetrachloride cannot be hydrolysed with water.
- (v) SnCl<sub>2</sub> is a solid while SnCl<sub>4</sub> is a liquid at room temperature.

#### 4. Answer the following:

PRACTICE PROBLEMS

- (a) Which is the basic building unit of all silicates?
- (b) Why are carbon compounds relatively inert?
- (c) What is dry ice? Why is it so called?

- (d) Why is diamond a bad conductor of electricity but a good conductor of heat?
- (e) Which halide of carbon is used as a refrigerant?

## 5. Indicate the principal ingredients of the following:

(a) Coal gas

[M.L.N.R. 1991]

(b) Producer gas

[M.L.N.R. 1991]

(c) Water gas

[M.L.N.R. 1991]

- (d) Natural gas
- (e) Soft glass
- (f) Hard glass

#### 6. What happens when the following are heated?

- (a) Red lead
- (b) Lead nitrate
- (c) Lead acetate
- (d) Hydrated stannous chloride
- (e) White lead

#### 7. What happens when?

- (i) Dilute nitric acid is slowly reacted with tin.
- (ii) Carbon dioxide is passed through a suspension of limestone in water. [I.I.T. 1991]
- (iii) Carbon and steam are heated.
- (iv) Red lead is treated with nitric acid. [M.L.N.R. 1992]
- (v) Iodine is added to stannous chloride.
- (vi) Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia.
- (vii) Tin is treated with concentrated nitric acid.
- (viii) Lead is obtained from galena by air reduction.
- (ix) NaOH solution is added to SnCl2 solution.
- (x) Silica is heated with CaF<sub>2</sub> and conc. H<sub>2</sub>SO<sub>4</sub>.
- (xi) Stannous chloride reacts with ferric chloride.
- (xii) Stannous chloride reacts with mercuric chloride.
- (xiii) SnS reacts with yellow ammonium sulphide.
- (xiv) Lead is reacted with acetic acid in presence of oxygen.
- (xv) Nitrobenzene is treated with acidified stannous chloride.
- (xvi) Methyl chloride is passed over powdered silicon in the presence of copper catalyst at 275–375°C.
- (xvii) Potassium ferrocyanide is heated with conc. H<sub>2</sub>SO<sub>4</sub>.
- (xviii) Carbon monoxide is passed over nickel at 80°C.
- (xix) Silicon is fused with soda ash.
- (xx) Lead chloride is heated with conc. HCl.

#### 8. How will you prepare the following?

- (i) Tin metal from cassiterite.
- (ii) Litharge from red lead.
- (iii) Red lead from litharge.
- (iv) White lead from lead.
- (v) Stannous oxide from stannous chloride.
- (vi) Silanes from silicon.
- (vii) Crystalline silicon from silicon tetrachloride.
- (viii) Tetraethyl lead from sodium lead alloy.
- (ix) Chrome yellow from litharge.
- (x) Carbon monoxide from water gas.

#### 9. Answer the following:

- (i) Which elements have the electronic configuration  $ns^2 np^2$ ? Give their names.
- (ii) What is chemical formula of soft glass?
- (iii) What is gas carbon?

- (iv) What are carburetted water gas and semiwater gas?
- (v) What is a metal carbonyl?
- (vi) What is tin disease or tin plague?
- (vii) How does SiCl<sub>4</sub> differ from CCl<sub>4</sub>?
- (viii) What is plumbosolvency?
- 10. Write short notes on the following:
  - (i) Structure of diamond (ii) Structure of graphite
  - (iii) Alloys of tin
- (iv) Fuel gases
- (v) Silicones
- (vi) Various forms of coal
- (vii) Fire extinguisher
- (viii) Catenation
- 11. Explain the following with proper reasoning.
  - (i) Carbon dioxide does not support combustion but a burning magnesium ribbon continues to burn in it.

[Hint: Mg reduces CO<sub>2</sub> to carbon,

$$2Mg + CO_2 \longrightarrow 2MgO + C$$
  
and therefore continues to burn in  $CO_2$ .

(ii) Graphite is a conductor but diamond is not a conductor.

**[Hint :** Graphite has layer structure in which each carbon is  $sp^2$  hybridized.  $\pi$ -electrons are delocalised and conduct electricity. In diamond each carbon is  $sp^3$  hybridized and no mobile or delocalised electrons are available.]

(iii) Carbon tetrachloride is not affected but silicon tetrachloride is hydrolysed by water.

[**Hint**: In silicon *d*-orbitals are available, *i.e.*, it increases its coordination number to 6.

$$\begin{array}{c|c}
Cl & Si & Cl + 2H_2O \longrightarrow H \\
Cl & Si & Cl + 2H_2O \longrightarrow H
\end{array}$$

$$\begin{array}{c|c}
Cl & Cl & Cl \\
Cl & Cl & Cl
\end{array}$$

$$\begin{array}{c|c}
Cl & Cl & Cl \\
H & Cl & Cl
\end{array}$$

$$\begin{array}{c|c}
Cl & Cl & Cl
\end{array}$$

$$\begin{array}{c|c}
Cl & Cl
\end{array}$$

$$\begin{array}{c|c}
Cl & Cl
\end{array}$$

$$\begin{array}{c|c}
Cl & Cl
\end{array}$$

$$\begin{array}{c|c}
Cl & Cl
\end{array}$$

In carbon d-orbitals are not present.]

(iv) Dilute HCl is preferred to dilute H<sub>2</sub>SO<sub>4</sub> for the preparation of carbon dioxide from marble.

[**Hint**: In case of dilute H<sub>2</sub>SO<sub>4</sub>,CaSO<sub>4</sub> is formed. This is deposited on the surface of marble and acts as a protective layer. This layer stops the further reaction to liberate CO<sub>2</sub>.]

(v)  $\operatorname{Sn}^{2+}$  and  $\operatorname{Fe}^{3+}$  cannot coexist in the same solution.

[Hint: Redox reaction occurs.

$$2Fe^{3+} + Sn^{2+} \longrightarrow Sn^{4+} + 2Fe^{2+}$$
.

(vi) CCl<sub>4</sub> is used as fire extinguisher but not CS<sub>2</sub>.

[**Hint**: CCl<sub>4</sub> is heavy non-combustible liquid but CS<sub>2</sub> is highly combustible liquid.

$$2CS_2 + 5O_2 \longrightarrow 2CO + 4SO_2$$

(vii) Sn is used in making solder.

[Hint: It is easily fusible alloying metal.]

(viii) The lead of lead pencils is not lead but graphite.

[**Hint**: Graphite has the property of marking paper.]
(ix) PbO does not dissolve in H<sub>2</sub>SO<sub>4</sub> while SnO is soluble in H<sub>2</sub>SO<sub>4</sub>.

[Hint: PbSO<sub>4</sub> is insoluble while SnSO<sub>4</sub> is soluble in water.]

(x) Alkali cannot be stored in a Sn or Pb vessel.

[Hint: Sn and Pb dissolve in alkali.]

(xi) Alkanes are more stable than silanes.

[Hint: The C—C bond energy is higher than Si—Si bond energy.]

(xii) CCl<sub>4</sub> does not act as a Lewis acid while SiCl<sub>4</sub> and SnCl<sub>4</sub> act as Lewis acids.

[Hint: SiCl<sub>4</sub> and SnCl<sub>4</sub> act as Lewis acids as they can extend their coordination number beyond 4 due to the presence of *d*-orbitals.]

(xiii) Radioactive materials are shielded by lead blocks.

[Hint: The penetration of radioactive rays is minimum through lead.]

(xiv) SnCl<sub>2</sub> has high melting point (is solid) while SnCl<sub>4</sub> has low melting point (is a liquid).

[Hint: SnCl<sub>2</sub> has ionic nature while SnCl<sub>4</sub> is a covalent compound involving sp<sup>3</sup> hybridization.]

(xv) Lead pollution is caused by car exhaust.

[Hint: Lead tetraethyl is added to petrol as antiknock. It is evolved during ignition of petrol as lead tetrabromide which causes pollution.]

(xvi) Carbon atom is tetravalent inspite of the fact that there are only two unpaired electrons in it.

**[Hint :** One of the *p*-orbitals is empty. The *ns* electron pair is unpaired and the electron is shifted to *np* orbital, *i.e.*, in excited state, the electronic configuration is  $2s^1 2p_x^1 2p_y^1 2p_z^1$ . There is  $sp^3$  hybridization and four hybrid orbitals each having one electron come into existence, showing tetravalency.]

(xvii) PbCl<sub>4</sub> exists while PbBr<sub>4</sub> and PbI<sub>4</sub> do not exist.

[Hint: Pb<sup>4+</sup> is an oxidising agent and readily changes into Pb<sup>2+</sup>. The Br<sup>-</sup> and Γ ions are reducing agents. Thus, redox reaction occurs indicating that PbBr<sub>4</sub> and PbI<sub>4</sub> are unstable compounds.

$$Pb^{4+} + 4Br^{-} \longrightarrow PbBr_2 + Br_2$$

(xviii)  $CO_2$  is an acidic anhydride while  $PbO_2$  is basic anhydride.

[**Hint**: C is a non-metal. Its oxide, CO<sub>2</sub>, is thus acidic in nature while lead is a metal and its oxide is basic in nature.]

**12.** A substance (X) is dissolved in concentrated hydrochloric acid and on treating the solution with sodium hydroxide solution a white precipitate formed which dissolved in excess, giving a solution with strongly reducing properties.

On heating (X) with sulphur, a brown powder (Y) was formed which dissolved in yellow ammonium sulphide and on adding HCl, a yellow precipitate was formed.

When (X) was strongly heated in air, a white powder (Z) was obtained. When (Z) was fused with sodium hydroxide and extracted with hot water, white crystals were obtained. Identify (X), (Y) and (Z) and write the reactions.

13. An inorganic compound (A) is a strong reducing agent. Its hydrolysis in water gives a white turbidity (B). Aqueous solution of (A) gives a white precipitate (C) with NaOH solution which is soluble in excess of NaOH. (A) reduces auric chloride to produce purple of cassius. (A) also reduces iodine and gives chromyl chloride test. What are (A) to (C) and give the chemical reactions.

[Ans. (A) = 
$$SnCl_2$$
; (B) =  $Sn(OH)Cl$ ; (C) =  $Sn(OH)_2$   
 $SnCl_2 + H_2O \longrightarrow Sn(OH)Cl + HCl$   
(A) (B)  
 $SnCl_2 + NaOH \longrightarrow Sn(OH)_2 + 2NaCl$   
(C)  
 $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$   
 $3SnCl_2 + 2AuCl_3 \longrightarrow 3SnCl_4 + 2Au$   
 $SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI$ 

14. A colourless crystalline solid (BA) dissolves in water. When the solid is heated with concentrated  $H_2SO_4$ , a reddish brown gas (X) is liberated. A solution of the salt when treated with potassium chromate solution gives a yellow precipitate (Y) insoluble in acetic acid. The same solution gives a white precipitate which dissolves in excess of NaOH to form a compound (Z). Identify (X), (Y), (Z) and the salt (BA).

[Ans.  $(BA) = Pb(NO_3)_2$ ;  $(X) = NO_2$ ;  $(Y) = PbCrO_4$ ;  $(Z) = Na_2PbO_2$ ]

5. A white solid (A) is not completely soluble in dilute HCl or

15. A white solid (A) is not completely soluble in dilute HCl or dilute H<sub>2</sub>SO<sub>4</sub> but dissolves in dilute HNO<sub>3</sub> with effer-vescences. In the evolved gas, a burning magnesium ribbon-continues to burn. (A) when heated forms a yellow solid (B) which is an amphoteric oxide. (B) when heated in air forms a red coloured compound (C). (C) when dissolved in concentrated HNO<sub>3</sub> gives a brown residue (D). Identify (A) to (D).

[Ans. (A) = 
$$PbCO_3$$
; (B) =  $PbO$ ; (C) =  $Pb_3O_4$ ; (D) =  $PbO_2$ ]

- **16.** A white coloured inorganic salt (A) gives the following reactions:
  - (i) It is soluble in water and the solution has sweet taste. The solution turns black in presence of  $H_2S$ .
  - (ii) The solution gives a white precipitate with dilute HCl which is soluble in hot water.
  - (iii) The salt when heated gives acetone and a yellow coloured residue.

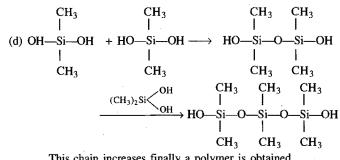
Identify the salt (A) and give chemical reactions.

[Ans. (A) is  $Pb(CH_3COO)_2$ 

$$\begin{array}{c} Pb(CH_3COO)_2 \,+\, H_2S \longrightarrow PbS \,+\, 2CH_3COOH \\ Black \\ Pb(CH_3COO)_2 \,+\, 2HCl \longrightarrow PbCl_2 \,+\, 2CH_3COOH \\ Soluble \ in \\ hot \ water \\ Pb(CH_3COO)_2 \longrightarrow PbO \,+\, CO_2 \,+\, CH_3COCH_3] \end{array}$$

- 17. Starting from SiCl<sub>4</sub> prepare the following in steps not exceeding the number given in parentheses (give reactions only):
  - (i) Silicon (I).
  - (ii) Linear silicon containing methyl groups only (4).
  - (iii) Na<sub>2</sub>SiO<sub>3</sub>(3). [I.I.T. 2001]

$$\begin{split} & [\textbf{Hint:} (i) \qquad SiCl_4 + 2Mg \longrightarrow Si + 2MgCl_2 \\ & (ii) \quad (a) \; SiCl_4 + 2Mg \longrightarrow Si + 2MgCl_2 \\ & \quad (b) \; Si + 2CH_3Cl \; \frac{Cu \; Catalyst}{280^\circ - 300^\circ C} \; (CH_3)_2 \; SiCl_2 \end{split}$$



This chain increases finally a polymer is obtained.

(iii) (a) 
$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

(b) 
$$Si(OH)_4 \xrightarrow{Heat} SiO_2 + 2H_2O$$

(c) 
$$SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2$$

#### Matching Type Questions

#### Match the following:

- [A] (a) Red lead
- (i) Carbon
- (b) Litharge
- (ii) An ore of tin
- (c) Galena
- (iii) A white pigment

- (d) Cassiterite
- (e) Lignite
- (f) White lead
- (g) Chrome yellow
- (h) Chrome red
- [B] (a) Diamond
  - (b) Graphite
  - (c) Phosgene

  - (d) Producer gas
  - (e) Water glass
  - (f) Carbon monoxide
  - (g) Solid carbon dioxide
  - (h) Carbon dioxide gas
- [C] (a)  $SnCl_4.5H_2O$ 
  - (b) (CH<sub>3</sub>COO)<sub>2</sub>Pb
  - (c) PbO<sub>2</sub>
  - (d) SiC
  - (e) SnCl<sub>2</sub>
  - (f) Solder
  - (g) Silanes
  - (h) Na<sub>2</sub>O·CaO·6SiO<sub>2</sub>

- (iv) PbCrO<sub>4</sub>
- (v) Lead monoxide
- (vi) PbCrO<sub>4</sub>·PbO
- (vii) Minium
- (viii) An ore of lead
  - (i) A poisonous gas
  - (ii) Metal carbonyls
- (iii) A fuel
- (iv) Fire extinguisher
- (v) Refrigerant
- (vi) Lead pencils
- (vii) Sodium silicate
- (viii) Abrasive
  - (i) Carborundum
  - (ii) An alloy of tin and lead
- (iii) Soda glass
- (iv) Hydrides of silicon
- (v) Butter of tin
- (vi) An oxidising agent
- (vii) Sugar of lead
- (viii) A reducing agent

### tuswers

#### Answers: Subjective Type Questions

- 1. (a) Diamond, graphite and coal. Graphite is a good conductor of electricity.
  - (b) Fullerene or Bucky ball
  - (c) <sup>14</sup><sub>6</sub>C (used for carbon dating)
- (d) Diamond.
- 2. (a) Carbon
  - (b) Lead
  - (c) Ununquadium (114)
  - (d) Silicon
  - (e) Silicon and germanium
- (f) Lead
- 3. (i) Due to inert pair effect.
  - (ii) Methane. Silicon atom is bigger in size in comparison to hydrogen, thus, silane is unstable.
  - (iii) Carbonates of alkali metals are salts of strong bases and weak acid and hence undergo hydrolysis.
  - (iv) The maximum covalency of carbon is 4 due to absence of d-orbitals. It cannot expand its octet.
  - (v) SnCl<sub>2</sub> is an ionic compound while SnCl<sub>4</sub> is covalent in nature.
- (a) SiO<sub>4</sub><sup>4-</sup> is the basic building unit of all silicates.
  - (b) Carbon-carbon bond dissociation energy is quite high.
  - (c) Solid carbon dioxide, it does not wet the surface when it melts.
  - (d) Mobile electrons are not present in diamond. Conduction of electricity requires movement of electrons. The conduction of heat does not require movement of electrons.
  - (e) Freon, CF<sub>2</sub>Cl<sub>2</sub>.
- 5. (a) Coal gas—H<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>
  - (b) Producer gas—CO, N<sub>2</sub>
  - (c) Water gas-CO, H2
  - (d) Natural gas-CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>

- (e) Soft glass-Na2O, CaO, SiO2
- (f) Hard glass-K2O, CaO, SiO2
- 6. (a) On heating above 470°C, it decomposes into PbO and O2-

$$2Pb_3O_4 \longrightarrow 6PbO + O_2$$

(b) On heating, it breaks up into PbO, NO2 and O2.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

(c) On heating, it decomposes giving acetone.

$$(CH_3COO)_2Pb \longrightarrow PbO + CO_2 + CH_3COCH_3$$

(d) Hydrolysis occurs with water of crystallisation.

$$SnCl_2 \cdot 2H_2O \longrightarrow Sn(OH)C1 + HC1 + H_2O$$

 $Sn + 10HNO_3(dil.) \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O_3$ 

(e) On heating, it decomposes into red lead,

$$2PbCO_3 \cdot Pb(OH)_2 \longrightarrow Pb_3O_4 + CO + CO_2 + H_2$$

$$2HNO_3 + 8H \longrightarrow NH_4NO_3 + 3H_2O$$

(ii) Limestone dissolves in the form calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

(iii) Water gas is formed.

$$C + H_2O \longrightarrow \underbrace{CO + H_2}_{Water\ gas}$$

(iv) 
$$Pb_3O_4 \longrightarrow 2PbO + PbO_2$$

$$[PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O] \times 2$$

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O_3$$

(v) It decolourises iodine.

$$2SnCl_2 + 2I_2 \longrightarrow 2SnCl_2I_2 \longrightarrow SnCl_4 + SnI_4$$

(vi) 
$$NH_4OH + CO_2 \longrightarrow NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

$$NaCl + NH_4OH + CO_2 \longrightarrow NaHCO_3 + NH_4Cl$$

$$\begin{array}{cccc} (vii) & & [2HNO_3 & \longrightarrow & H_2O + 2NO_2 + O] \times 2 \\ & & \underline{Sn + 2O + H_2O \longrightarrow & H_2SnO_3} \\ & & & \underline{Sn + 4HNO_3 \longrightarrow & H_2SnO_3 + 4NO_2 + H_2O} \\ & & & \underline{Metastannic \ acid} \end{array}$$

(viii) 
$$2PbS + O_2 \longrightarrow 2PbO + SO_2$$
  
 $PbS + 2O_2 \longrightarrow PbSO_4$ 

Roasted in a limited supply of oxygen. Air supply is cut-off and fresh galena is added and the temperature is raised. Galena reduces both PbO and PbSO<sub>4</sub> to metallic lead.

$$2PbO + PbS \longrightarrow 3Pb + SO_2$$

$$PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2$$

(ix) 
$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$$
  
 $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$ 

$$\frac{2}{\text{SnCl}_2 + 4\text{NaOH} \longrightarrow \text{Na}_2\text{SnO}_2 + 2\text{NaCl} + 2\text{H}_2\text{O}}$$

(x) 
$$[CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF] \times 2$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$2CaF_2 + SiO_2 + 2H_2SO_4 \longrightarrow 2CaSO_4 + SiF_4 + 2H_2O$$

$$SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$$

(xii) 
$$HgCl_2 + SnCl_2 \longrightarrow Hg + SnCl_4$$

(xiii) 
$$SnS + S \longrightarrow SnS_2$$

$$SnS_2 + (NH_4)_2S \longrightarrow (NH_4)_2SnS_3$$

(xiv) Pb + 2CH<sub>3</sub>COOH + 
$$\frac{1}{2}$$
 O<sub>2</sub>  $\longrightarrow$  (CH<sub>3</sub>COO)<sub>2</sub>Pb + H<sub>2</sub>O

$$(xv) C_6H_5NO_2 + 6HCl + 3SnCl_2 \longrightarrow C_6H_5NH_2 + 3SnCl_4 + 2H_2O$$

(xvi) 
$$2CH_3Cl + Si \xrightarrow{Cu} (CH_3)_2SiCl_2$$

$$(xvii)K_4Fe(CN)_6 + 3H_2SO_4 \longrightarrow 2K_2SO_4 + FeSO_4 + 6HCN$$

$$[HCN + 2H_2O \longrightarrow HCOOH + NH_3] \times 6$$

$$[2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4] \times 3$$

$$[HCOOH \longrightarrow CO + H_2O] \times 6$$

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 +$$

$$3(NH_4)_2SO_4 + 6CO$$

(xviii) Ni + 4CO 
$$\longrightarrow$$
 Ni(CO)<sub>4</sub>

Nickel carbonyl

(xix) 
$$Si + Na_2CO_3 \longrightarrow Na_2SiO_3 + C$$

$$\begin{array}{ccc} \text{(xx)} & & \text{PbCl}_2 + 2\text{HCl} & \longrightarrow & \text{H}_2\text{PbCl}_4 \\ & & \text{Chloroplumbous acid} \\ & & \text{(Soluble)} \end{array}$$

3. (i) The ore is first roasted to remove sulphur, arsenic as SO<sub>2</sub> and As<sub>2</sub>O<sub>3</sub> respectively. The roasted mass is mixed with about one fifth its mass of powdered anthracite and a little lime. The mixture is heated in reverberatory furnace when tin metal is formed.

$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

(ii) On heating above 470°C, red lead decomposes into litharge.  $2Pb_3O_4 \longrightarrow 6PbO + O_2$ 

(iii) On heating litharge in air about 450°C.

$$6PbO + O_2 \longrightarrow 2Pb_3O_4$$

- (iv) Lead is converted into white lead by Dutch process or electrolytic process. See text on page 436.
- (v) NaOH is added to stannous chloride. The stannous hydroxide precipitated is heated in atmosphere of CO<sub>2</sub>.

$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$$
  
 $Sn(OH)_2 \xrightarrow{Heat, CO_2} SnO + H_2O$ 

(vi) Silicon is fused with magnesium. Magnesium silicide is now treated with dilute HCl when a mixture of silicon hydrides is obtained.

$$2Mg + Si \longrightarrow Mg_2Si \xrightarrow{Dil. HCl} A$$
 mixture of silicon hydrides (Silanes)

(vii) By passing a current of silicon tetrachloride over molten aluminium.

$$3SiCl_4 + 4Al \longrightarrow 3Si + 4AlCl_3$$

(viii) 
$$4C_2H_5C_1 + 4Pb$$
—Na  $\longrightarrow (C_2H_5)_4Pb + 4NaC_1 + 3Pb$ 

(ix) PbO + 2CH<sub>3</sub>COOH 
$$\longrightarrow$$
 (CH<sub>3</sub>COO)<sub>2</sub>Pb + H<sub>2</sub>O  
(CH<sub>3</sub>COO)<sub>2</sub>Pb + K<sub>2</sub>CrO<sub>4</sub>  $\longrightarrow$  PbCrO<sub>4</sub> + 2CH<sub>3</sub>COOK  
Chrome yellow

x)  $\underbrace{\text{CO} + \text{H}_2}_{\text{Water gas}} \xrightarrow{200 \text{ atm.}}_{\text{Amm.Cu}_2\text{Cl}_2} \text{CO is absorbed.}$ 

It is released when pressure is removed.

- (i) Elements of IVA or 14th group : Carbon, Silicon, Germanium, Tin and Lead.
  - (ii) Na<sub>2</sub>SiO<sub>3</sub>·CaSiO<sub>3</sub>·4SiO<sub>2</sub>
  - (iii) The amorphous form of carbon obtained by scrapping the walls of a retort which has been used in destructive distillation of coal.
  - (iv) The water gas mixed with volatile hydrocarbons is known as carburetted water gas. Semiwater gas is a mixture of water gas and producer gas. It is obtained by passing a mixture of steam and air over incandescent coke.
  - (v) A coordination compound of metal with carbon monoxide molecules as ligands is known as metal carbonyl.
  - (vi) The crumbling of white tin into grey powder from a very low temperature is called tin disease or tin plague.
  - (vii) CCl<sub>4</sub> does not undergo hydrolysis while SiCl<sub>4</sub> undergoes hydrolysis.
  - (viii) The dissolution of lead in water in presence of dissolved oxygen is known as plumbosolvency.

12. 
$$X = Sn$$
;  $Y = SnS$ ;  $Z = SnO_2$ 

$$\operatorname{Sn} + 2\operatorname{HCl} \longrightarrow \operatorname{SnCl}_2 + \operatorname{H}_2$$
(X)

$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$$
  
 $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$ 

$$Sn + S \longrightarrow SnS$$
(Y) Brown

$$SnS + (NH4)2SnS2 \longrightarrow (NH4)2SnS3$$

$$(NH_4)_2SnS_3 + 2HCl \longrightarrow SnS_2 + H_2S + 2NH_4Cl$$

$$Sn + O_2 \longrightarrow SnO_2$$

$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$$

#### Answers: Matching Type Questions

## ILLUSTRATIONS OF OBJECTIVE QUESTIONS



- 1. Graphite is not:
  - (a) a good conductor of heat
  - (b) an amorphous allotrope of carbon
  - (c) softer than diamond:
  - (d) used for making lubricants

Ans. (b)

[Hint: Graphite is crystalline allotrope of carbon.]

- **2.** Carbon atoms in diamond are bonded with each other in a configuration :
  - (a) linear

(b) planar

(c) tetrahedral

(d) octahedral

Ans. (c)

- 3. When heated with concentrated H<sub>2</sub>SO<sub>4</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub> gives :
  - (a) CO

(b) CO<sub>2</sub>

(c) (CN)<sub>2</sub> and CO

(d)  $(CN)_2$  and  $CO_2$ 

Ans. (a)

[Hint:  $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$ ]

- 4. Carbon monoxide is absorbed by:
  - (a) plants
  - (b) alcohol
  - (c) Ni(CO)<sub>4</sub>
  - (d) ammonical solution of cuprous chloride

Ans. (d)

[Hint: All the four valencies of carbon are not satisfied. It behaves as an unsaturated compound and forms addition products.

$$\begin{array}{ccc} CuCl & + CO & \xrightarrow{High} & CuCl \cdot CO] \\ Ammonical & solution & & \end{array}$$

- 5. Which of the following is correct?
  - (a) Silicones are organosilico polymers containing Si—O—Si linkage.
  - (b)  $R_3$ SiCl on hydrolysis gives  $R_3$ Si—O—Si $R_3$
  - (c) Both
  - (d) None

Ans. (c)

- 6. The general formula of cyclic or ring silicates is:
  - (a)  $(Si_2O_5)_n^{2n}$

(b)  $(SiO_3)_n^{2n}$ 

(c)  $(SiO_3^{2-})_n$ 

(d) both (b) and (c)

Ans. (d)

- 7. Which one of the following statements is wrong?
  - (a) Ionic carbides are formed by highly electropositive metals.
  - (b) Carborundum and boron carbide are true covalent carbide.
  - (c) Carborundum and boron carbide are used as abrasive.
  - (d)  $Mg_2C_3$  like  $CaC_2$  on hydrolysis evolves  $C_2H_2$ .

Ans. (d)

[Hint:  $Mg_2C_3$  on hydrolysis evolves propyne.  $Mg_2C_3 + 4H_2O$  $\longrightarrow 2Mg(OH)_2 + CH_3-C = CH \text{ (propyne)}]$ 

- **8.** In  $(SiO_4)^{4-}$  (tetrahedral structure), three oxygen atoms are shared in which of the following? [I.I.T. 2005]
  - (a) Sheet silicates

(b) Three dimensional silicates

(c) Linear silicate

(d) Pyrosilicate

Ans. (a)

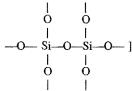
[Hint: See page No. 427]

9. In silicon dioxide:

[A.I.E.E.E. 2005]

- (a) each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms
- (b) each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
- (c) silicon atom is bonded to two oxygen atoms
- (d) there are double bonds between silicon and oxygen atoms. **Ans.** (a)

[Hint: Each silicon atom is surrounded tetrahedrally by four oxygen atoms.



10. Silica reacts with magnesium to form a magnesium compound (X). (X) reacts with dilute HCl and forms (Y). (Y) is:

[E.A.M.C.E.T. 2004]

(a) MgO

- (b) MgCl<sub>2</sub>
- (c) MgSiO
- (d) SiCl<sub>4</sub>

Ans. (b)

[Hint: 
$$SiO_2 + 2Mg \longrightarrow 2MgO + Si$$
;  $MgO + 2HCl \longrightarrow MgCl_2$ 

$$(X) \qquad (Y)$$

$$+ H_2O]$$

- 11. Silica is reacted with sodium carbonate. What is the gas liberated? [E.A.M.C.E.T. 2005]
  - (a) CO

(b) O<sub>2</sub>

(c) CO<sub>2</sub>

(d) O<sub>3</sub>

Ans. (c)

[Hint:  $SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2$ ]

12. Pb and Sn are extracted from their chief ores by:

[I.I.T. 2004]

- (a) carbon reduction and self reduction
- (b) self reduction and carbon reduction
- (c) electrolysis and self reduction
- (d) self reduction and electrolysis

Ans. (b)

[Hint: PbS + 2PbO  $\longrightarrow$  3Pb + SO<sub>2</sub> (self reduction); SnO<sub>2</sub> + C  $\longrightarrow$  Sn + CO<sub>2</sub> (carbon reduction)]

13. The soldiers of Napoleon army while at Alps during freezing winter suffered a serious problem as regards to tin buttons of their uniforms. White metallic buttons of tin got converted to grey powder. This transformation is related to:

[A.I.E.E.E. 2004]

- (a) an interaction with nitrogen of the air with very low temperature
  (b) an interaction with water vapour present in humid air
  (c) a change in the partial pressure of oxygen present in the air
  (d) a change in the crystalline structure of tin
  Ans. (d)
  [Hint: White tin converts itself into grey tin at 18°C.]
  14. Ge (II) compounds are powerful reducing agents whereas Pb (IV) compounds are strong oxidants. It can be due to:
  (a) Pb is more electronegative than Ge
  (b) ionisation potential of lead is less than that of Ge
- (c) ionic radii of Pb<sup>2+</sup> and Pb<sup>4+</sup> are larger than those of Ge<sup>2+</sup> and Ge<sup>4+</sup>
- (d) more pronounced inert pair effect in lead than in Ge.

Ans. (d)

**15.** Buckminsterfullerene is :

(a) graphite

(b) diamond

(c) C-60

(d) bone charcoal

Ans. (c)

[Hint: Fullerene, a carbon allotrope, consists of spherical C-60 molecules with the extra ordinary shape of a soccer ball. It has 12 pentagonal and 20 hexagonal faces with each atom  $sp^2$  hybridized and bonded to three other atoms.]

#### **OBJECTIVE QUESTIONS**



Set I:	This set	cont	ains	ques	stions	with	singl	le corr	ect answer.

1.	In the ground state the carbon atom has unpaired	10.	Which of the following is the chemically inactive allotre	opic
	electron/electrons:		form of carbon?	
	(a) 2 $\square$ (b) 3 $\square$	-	(a) diamond	$\Box$
	(c) 4 $\square$ (d) no $\square$		(c) charcoal	
2.	What is the general electronic configuration of group 14 or	11.	The use of diamond as a gem depends on its:	
	IVA elements:		(a) hardness $\square$ (b) high refractive index	
	(a) $ns^2 np^4$		(c) purest form of carbon □ (d) chemical inertness	
		12.	CO forms a volatile compound with:	
3.	The element which forms only one hydride is:		(a) nickel	
	(a) C $\square$ (b) Si $\square$		(c) sodium	
	(c) Pb $\Box$ (d) none of these $\Box$	13.	A colourless gas which burns with blue flame and red	uces
4.	Carbon shows tetravalency due to:		CuO to Cu is:	
	(a) $s^2p^2$ hybridization $\square$ (b) $d^3p$ hybridization $\square$		(a) $N_2$	
	(c) $dsp^2$ hybridization $\Box$ (d) $sp^3$ hybridization $\Box$		(c) $CO_2$	
5.	In group IVA or 14 of the extended form of the periodic table	14.	Fire extinguishers contain a bottle of H <sub>2</sub> SO <sub>4</sub> and:	
	with increase in atomic number, the metallic character:		(a) CaCO <sub>3</sub>	
	(a) increases		(c) NaHCO <sub>3</sub>	
-	(b) decreases	15	$H_2SO_4$ is not used for the preparation of $CO_2$ from ma	
	(c) remains the same	13.	chips because:	1010
_	(d) first increases then decreases	}	(a) it does not react	
6.	The species present in solution when CO <sub>2</sub> is dissolved in		(b) huge amount of heat is evolved	
	water:		(c) the reaction is vigorous	
	(a) $H_2CO_3, CO_3^{2-}$	ļ	(d) calcium sulphate is sparingly soluble and get depos	
	(b) HCO <sub>3</sub> , CO <sub>3</sub> <sup>2</sup>		on marble chips and stops the reaction	,nca
	(c) CO <sub>2</sub> , H <sub>2</sub> CO <sub>3</sub>	16	Producer gas is the mixture of:	. –
	\-\(\frac{1}{2}\) - \(\frac{1}{2}\) - \(\frac{1}{2}\) - \(\frac{1}{2}\) - \(\frac{1}{2}\) - \(\frac{1}{2}\) - \(\frac{1}{2}\)	10.	(a) CO and $N_2$	
	[Hint: $CO_2 + H_2O \Longrightarrow H_2CO_3 \Longrightarrow H^+ + HCO_3^- \Longrightarrow 2H^+ + CO_3^{2-}$ ]		(c) $N_2$ and $NH_3$ $\square$ (d) $CO$ , $H_2$ and $N_2$	
7	Diamond and graphite are:	17	A dry ice piece is composed of:	
/.	(a) isomers	17.		
	(c) isotopes		(a) solid He $\Box$ (b) solid $CO_2$ (c) solid $SO_2$ $\Box$ (d) solid $C_6H_6$	
R	Carbon has valency four in CH <sub>4</sub> . Its valency in acetylene is:	18	In laboratory burners, we use:	
0.	(a) 1	10.	(a) producer gas $\Box$ (b) coal gas	
	(c) 3 $\square$ (d) 4 $\square$			
9	Which of the following is a good conductor of electricity?	10	(c) oil gas	
٦.	(a) diamond $\Box$ (b) graphite $\Box$	19	Maximum ability of catenation is shown by:	
	(c) coal $\Box$ (d) none of these $\Box$		(a) carbon ☐ (b) nitrogen ☐ (c) oxygen ☐ (d) sulphur	
	(a) none of those	1	(c) oxygen	

20.	Graphite is a good conductor of electricity because it	32.	The structure and hybridization of Si(CH <sub>3</sub> ) <sub>4</sub> is:	
	contains:		\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	]
	(a) bonded electrons $\Box$ (b) mobile electrons $\Box$		(c) octahedral, $sp^3d^2$ $\square$ (d) tetrahedral, $sp^3$ $\square$	
	(c) strong C—C bonds □ (d) strong C=C bonds □	33.	Among the following substituted silanes, the one which wi	11
21.	Which form of the carbon has a two dimensional sheet like	:	give rise to cross linked silicone polymer on hydrolysis is	:
	structure?		(a) $RSiCl_3$ $\square$ (b) $R_4Si$	]
	(a) Diamond		(c) $R_2 \text{SiCl}_2$	]
	(c) Graphite	34.	Structural units of ice and dry ice are respectively:	
22.	If CO <sub>2</sub> is passed in excess into lime water, the milkiness first		(a) $H_2O$ , $CO$ $\Box$ (b) $CO_2$ , $H_2O$	]
	formed disappears due to:		(c) $H_2O, CO_2$ $\square$ (d) $CO, CO_2$	
	(a) reversal of the original reaction	35.	Which of the following is a semiconductor?	
	(b) formation of volatile calcium derivative			
	(c) formation of water soluble calcium bicarbonate	- 1	(c) Ge	J
	(d) the solution getting heated by exothermic reaction	1 00	Carbon atoms in diamond are bonded with each other in	a
23.	When steam is passed through red hot coke:		configuration:	
۵.	(a) CO <sub>2</sub> and H <sub>2</sub> are obtained		(a) linear	
	(b) CO and N <sub>2</sub> are formed		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	
	* *	1 27		
		<b>.</b>		3-
~4	(d) petrol gas is obtained	'		_
24.	Glass could be considered as:		(c) it is neither combustible nor a supporter of combustion	
	(a) amorphous solid	1		ה ר
	(c) crystalline solid $\Box$ (d) super cooled liquid $\Box$		(d) it is a colourless gas	_
25.	An important ore of lead is:	38	— · · · · · · · · · · · · · · · · · · ·	_
	(a) magnesite	50	expansion is:	
	(c) bauxite			
26.	Glass is soluble in:			_
	(a) HF $\square$ (b) H <sub>2</sub> SO <sub>4</sub> $\square$	30	When the destructive distillation of coal is done, the	
	(c) HClO <sub>4</sub>		non-volatile residue left in the retort is:	ıc
27.	An alloy which does not contain copper is:			_
	(a) bell metal			_
	(c) brass	40		_
28.	Coal gas is a mixture of:	1.40	gives more of:	g
	(a) CO and H <sub>2</sub>			7
	(b) H <sub>2</sub> , saturated and unsaturated hydrocarbons, CO, CO <sub>2</sub>	.	* *	
	$N_2$ and $O_2$	. 1	For complete combustion of a fuel we shall need:	
	(c) saturated and unsaturated hydrocarbons	41	<del>-</del>	_
	(d) CO, CO <sub>2</sub> and CH <sub>4</sub>		( )	
29.	[SiO <sub>4</sub> ] <sup>4-</sup> has tetrahedral structure, the silicate formed by using	1		<u></u>
	three oxygen has a:	'		
	(a) linear polymeric structure	I <sub>42</sub>		_
	(b) three dimensional structure	1		7
	(c) pyrosilicate structure	1		_
	(d) two dimensional sheet structure		* •	
30.	Coal gas:	<b>'</b>	* * *	
50.		1 40		
	(a) burns with a smoky flame	. 1	Colour is imparted to glass by mixing:	_
	(b) burns with non-smoky flame	_		_
	(c) is not used for lighting purposes	į.	* *	
	(d) is not a good fuel	I   44		
31.	Mark the correct statement:	.	J.E.E. (Orissa) 2010	_
	(a) Water gas is used in the manufacture of methyl alcoho	. !	`/ +	_
	(b) Water gas has the highest calorific value	1	The poisonous gas present in the exhaust fumes of car is	_
	(c) Water gas burns with luminous flame			_
	(d) The production of water gas is exothermic process.	1 (	(c) carbon monoxide	

46.	Phosgene is the common name given to:	_		(d) it has strong catenation property	
	(a) carbonyl chloride	빌ㅣ	61.	The heat of combustion of carbon is 94 kcal. The calori	tic
	(c) phosphorus oxychloride			value of carbon is about:	_
	(d) phosphorus trichloride			_ (5) 1515 1515	
47.	Red lead is:	_	<i>(</i> 2	_ (4)	
	(a) PbO $\square$ (b) PbO <sub>2</sub>		62.	Which compound is called sugar of lead?	_
	(c) $Pb_3O_4$			(a) $PbCl_2$	
48.	Which of the following halides is least stable and h	nas	· .	(5) 10004	
	doubtful existence?	_	63.	The number and type of bonds between two carbon ator	ms
	(a) $CI_4$			in CaC <sub>2</sub> are:	_
	(c) $GeI_4$			(a) one sigma and one pi bond	닏
49.	Which one of the oxides is neutral?	_ 1		(b) one sigma and two pi bonds	
	(a) CO $\square$ (b) SnO <sub>2</sub>			(c) one sigma and one and a half pi bond	
	(c) $ZnO$ $\Box$ (d) $SiO_2$			(d) one sigma bond	
50.	An example of major air pollutant is:	_	64.	When a mixture of air and steam is passed over red hot col	ke,
	(a) $O_2$			the outgoing gas contains:	
	(c) CO			()	
51.	*			(c) coal gas	
	(a) it combines with water to give carbonic acid		65.	Tin reacts with conc. HNO <sub>3</sub> and gives:	_
	(b) it combines with haemoglobin of the blood			(a) stannic nitrate	
	(c) it is a powerful oxidising agent			(c) metastannic acid	
	(d) it is used to prepare aerated water		66.	Which substance is used as lubricant?	_
52.	Which of the following compounds is used as a reduc-	ing		(a) $SnCl_2$	
	agent?		/	(c) graphite	
	(a) $SnO_2$ $\square$ (b) $SnS_2$		67.	The colour imparted by Co(II) compounds to glass is:	
	(c) $SnCl_4$			[A.I.I.M.S. 20	06J
53.	Which of the following statements is not correct?			(a) deep blue	님
	(a) Lead salts are slow poisons		<b>CO</b>	(c) yellow	
	(b) Lead metal is used in accumulators		68.	The principal constituent of pyrex glass is:	_
	(c) Plumbosolvency increases by the presence of car			(a) Zn	
	nates, sulphates, phosphates, etc.		<b>40</b>	(c) Pb	
~.	(d) Lead is a soft metal		69.	The difference in properties of $CH_4$ and $SiH_4$ is due to:	
54.	Chrome yellow is chemically called:	_		(a) large difference in the electronegativity of carbon a	ana
	(a) lead chromate			silicon	
	(c) lead iodide		l I	(b) large difference in size of carbon and silicon atoms	
55.				(c) the inability of carbon to expand its octet	
	(a) Pb(OH) <sub>2</sub> ·PbCO <sub>3</sub>		70	(d) the inability of silicon to form double bonds	
56	(c) Pb(OH) <sub>2</sub> ·Pb(CH <sub>3</sub> COO) <sub>2</sub> (d) PbCO <sub>3</sub> ·PbO		70.		IIO-
56.	<b>-</b>			lysed because:	and
	(a) $CaC_2$ $\square$ (b) $Al_4C_3$ (c) $WC$ $\square$ (d) $SiC$			(a) carbon cannot expand its octet but silicon can expa	П
57		ш		its octet  (b) ionication potential of carbon is higher than silicon.	
57.				<ul><li>(b) ionisation potential of carbon is higher than silicon</li><li>(c) carbon forms double and triple bonds</li></ul>	
				(d) electronegativity of carbon is higher than that of silic	COD
58.	(c) $C_3O_2$			(d) electronegativity of carbon is nigher than that of sine	
50.	sodium hydroxide solution:	O)	71	Which of the following oxides has three dimension	mal
	(a) $Fe^{3+}$		/1.	structure?	niai
	(a) Fe $\square  (b) \text{ C1}$ (c) $\text{Sn}^{2+} \qquad \square  (d) \text{ Cu}^{2+}$			() 65	
50		LI			
59.	(a) Na <sub>2</sub> O		72.	(c) SiO <sub>2</sub>	
	(a) $Na_2O$ $\square$ (b) $NO$ (c) $CaO$ $\square$ (d) $SnO$		12.	This shows that carbon has:	<b>℃</b> 2.
60.				(a) two allotropic forms	
ω.	(a) carbon is tetra-valent	<del>:.</del> □		(b) two oxidation states	
	(b) it has non-metallic character			(c) two oxidation states	
	(c) it shows allotropy			(d) four electrons in valency shells	
	THE AS DALOTTO MILITARY		1	in ton continue in the city diffin	-

73.	In silicon dioxide:	86.	Solder is an alloy of: [A.F.M.C. 20	005]
	(a) there are double bonds between silicon and oxygen		(a) 70 % Pb, 30 % Sn	
	atoms		(c) 80 % Pb, 20 % Sn	
	(b) each silicon atom is surounded by four oxygen atoms	87.	Solid carbon dioxide is used as:	
	and each oxygen atom is bonded to two silicon atoms		(a) poison	
			(c) refrigerant	
	(c) silicon is bonded to two silicon atoms $\Box$	88.	When PbO <sub>2</sub> reacts with conc. HNO <sub>3</sub> , the gas evolved is	s:
	(d) each silicon atom is surrounded by two oxygen atoms		[A.I.E.E.E. 20	105]
	and each oxygen atom is bonded to two silicon atoms	<u>.</u>	(a) $NO_2$	
			(c) $N_2$	
74.	In the manufacture of glass the addition of MnO <sub>2</sub> gives:	89.	When steam reacts with red hot coke to form CO2 a	and
	(a) yellow colour $\Box$ (b) red colour $\Box$		hydrogen:	
	(c) violet colour $\Box$ (d) pink colour $\Box$		(a) water acts as oxidising agent	
<i>7</i> 5.	Which is not used as pigment in paints?		(b) water acts as reducing agent	
	(a) $PbCrO_4$ $\square$ (b) $PbO_2$ $\square$		(c) carbon acts as oxidising agent	
	(c) White lead $\Box$ (d) Pb <sub>3</sub> O <sub>4</sub> $\Box$		(d) there is no oxidation or reduction .	
76.	Lead dissolves most readily in:	90.	, .	
	(a) acetic acid $\Box$ (b) sulphuric acid $\Box$		(a) CO + steam $\Box$ (b) CO + N <sub>2</sub>	
	(c) nitric acid $\Box$ (d) hydrochloric acid $\Box$		(c) $CO + H_2$	
77.	Which of the following metals is an important ingredient of	91.	e; e	
	transistors?		(a) -Sn—Sn	
	(a) Osmium		(c) Si—Si	
	(c) Gold $\Box$ (d) Sodium $\Box$	92.	Graphite is soft and lubricant, extremely difficult to melt.	The
78.	The gas which is present both in producer gas and in water		reason for this anomalous behaviour is that graphite:	
	gas is:		[A.I.E.E.E. 20	
	(a) $N_2$ $\square$ (b) $H_2$ $\square$		(a) has carbon atoms arranged in large plates of rings	
	(c) CO $\square$ (d) CO <sub>2</sub> $\square$		strongly bound carbon atoms with weak interp	late
79.	Which glass has the highest percentage of lead?		bonds	
	(a) Soda glass $\Box$ (b) Flint glass $\Box$		(b) is a non-crystalline substance	
	(c) Jena glass $\Box$ (d) Pyrex glass $\Box$		(c) is an allotrope form of carbon	
80.	Which does not exist?		(d) has molecules of variable molecular masses polymers	
	(a) $[CCl_6]^2$	93.	Which of the following is correct composition of water g	
	(c) $[GeF_6]^{2-}$ $\Box$ (d) $[SnCl_6]^{2-}$ $\Box$	93.	(a) $CO + Cl_2$	
81.	The material used in solar cells contains:		(a) $CO + CI_2$ $\Box$ (b) $CO + II_2$ (c) $CO + H_2$ $\Box$ (d) $CO + H_2 + N_2$	
•	(a) Si $\Box$ (b) Sn $\Box$	94	What is the formula of carbon suboxide?	
	(c) Ti $\Box$ (d) Cs $\Box$	"	(a) CO $\Box$ (b) CO <sub>2</sub>	
82.	'Softening of lead' means:	ļ	(c) $C_2O_4$ $\square$ (d) $C_3O_2$	
*	(a) conversion of lead to PbO	95.	Which of the following halide of carbon is used	
	(b) conversion of lead to $Pb_3O_4$		refrigerant?	
	(c) removal of impurities (metallic) from lead		(a) $CCl_4$ $\Box$ (b) $CF_4$	
	(d) washing lead with HNO <sub>3</sub> followed by a dil. alkali	,	(c) $CH_2Cl_2$ $\square$ (d) $CH_2F_2$	
	solution	96.	The carbide which gives propyne on hydrolysis:	
83.	'Lead pencil' contains:		(a) $Al_4C_3$ $\Box$ (b) $CaC_2$	
	(a) graphite		(c) $Fe_3C$ $\Box$ (d) $Mg_2C_3$	
	(c) charcoal . □ (d) lead sulphide □	97.	Which among the following carbides is methanide?	
84.	Electrolytic bath in electrolytic refining of lead contains:		(a) $Al_4C_3$ $\Box$ (b) $CaC_2$	
	(a) $H_2SiF_6$ only		(c) $Be_2C$ $\square$ (d) $SiC$	
	(b) PbSiF <sub>6</sub> only $\Box$	98.	Percentage of lead in lead pencil is:	
	(c) H <sub>2</sub> SiF <sub>6</sub> in presence of gelatin		(a) zero	
	(d) $H_2SiF_6$ and $PbSiF_6$ in presence of gelatin		(c) 80	
85.	Which of the following oxides is amphoteric in character?	99.	CCl <sub>4</sub> is used as fire extinguisher because:	_
	[A.I.E.E.E. 2005]		(a) its m.pt. is high $\Box$ (b) it forms covalent bon	
	(a) CaO $\Box$ (b) CO <sub>2</sub> $\Box$		(c) its b.pt. is low	
	(c) $SiO_2$ $\Box$ (d) $SnO_2$ $\Box$	1	(d) it gives incombustible vapours	П

100.	The correct order of increasing C—O bond length of CO, $CO_3^{2-}$ , $CO_2$ is: [C.B.S.E. 2007]	112.	Which is likely to show inert pair effect?
	(a) $CO_3^{2-} < CO_2 < CO$		[D.C.E. (Engg.) 2007] (a) K
			(a) K $\square$ (b) Mg $\square$ (c) Al $\square$ (d) Pb $\square$
101	(c) $CO < CO_3^2 < CO_2$	113.	The stability of dihalides of Si, Ge, Sn and Pb increases
101.	PbF <sub>4</sub> , PbCl <sub>4</sub> exists but PbBr <sub>4</sub> and PbI <sub>4</sub> do not exist	115.	
	because of: [C.E.E. (Haryana) 2000]		•
	(a) large size of Br and I		(a) $PbX_2 < SnX_2 < GeX_2 < SiX_2$ (b) $GeX_2 < SiX_2 < SnX_2 < PbX_2$
	(b) strong oxidising character of Pb <sup>4+</sup>	ĺ	· · · · · · · · · · · · · · · · · · ·
	(c) strong reducing character of Pb <sup>4+</sup>		(6) 5212 ( 5512 ( 5512 ( 5512
100	(d) low electronegativity of Br and I   [A DNG 2001]		(d) $SiX_2 < GeX_2 < SnX_2 < PbX_2$
102.	Marsh gas contains: [A.F.M.C. 2001]	114.	Which of the following oxidation states are the most charac-
	(a) $CH_4$ $\square$ (b) $CO_2$ $\square$ (c) $C_2H_6$ $\square$ (d) $N_2$ $\square$		teristic for lead and tin respectively? [C.B.S.E, 2007]
103.			(a) +2, +4
105.	Which of the following is most stable? [C.P.M.T. 2001] (a) $\operatorname{Sn}^{2+}$ $\square$ (b) $\operatorname{Ge}^{2+}$ $\square$		(c) $+2, +2$
	(a) $\operatorname{Sn}^{2+}$ $\square$ (b) $\operatorname{Ge}^{2+}$ $\square$ (c) $\operatorname{Si}^{2+}$ $\square$ (d) $\operatorname{Pb}^{2+}$ $\square$	115.	Which one of the following is present in the chain structure
104			of silicates? [C.B.S.E. 2007]
104.	The state of the s		(a) $(Si_2O_5^2)_n$ $\square$ (b) $(SiO_3^2)_n$ $\square$
			(c) $(SiO_4)^{4-}$
105		116.	Which of the following has the highest calorific value?
105.	Biogas and producer gas are made up of:		[B.H.U. 2007]
	[B.V. (Pune) 2002] (a) biogas contains CO <sub>2</sub> but producer gas does not		(a) Coal gas
	2 1		(c) Producer gas
	(b) producer gas contains CO but not CO <sub>2</sub>	117.	The hybrid state of carbon atoms in C <sub>60</sub> molecule is:
	(c) both biogas and producer gas have $N_2$		(a) $sp$ $\square$ (b) $sp^3$ $\square$
100	(d) all the three above		(c) $dsp^2$ $\Box$ (d) $sp^2$ $\Box$
106.	Me <sub>2</sub> SiCl <sub>2</sub> on hydrolysis will produce: [I.I.T. (S) 2003]	118.	Litharge is chemically: [A.I.I.M.S. 2007]
	(a) $Me_2Si(OH)_2$		(a) PbO $\square$ (b) PbO <sub>2</sub> $\square$
	(b) $Me_2Si = O$		(c) $Pb_3O_4$
	(c) $-[-O-(Me)_2Si-O-]_n$	110	
107	(d) Me <sub>2</sub> SiCIOH	119.	$\operatorname{SiCl}_4 \xrightarrow{\operatorname{H}_2\operatorname{O}} X \xrightarrow{\operatorname{1000}} Y$
107.	Carborundum is: [B.H.U. 2003]		In the above reaction, X and Y respectively are:
	(a) $Al_2O_3$		[E.A.M.C.E.T. (Med.) 2007]
108.	Which of the following is the composition of solder?		(a) $SiO_2$ and $Si$
100.	[A.F.M.C. 2003]	120	(c) $H_2SiCl_6$ and $SiO_2$ $\square$ (d) $H_4SiO_4$ and $Si$ $\square$
	(a) $Cu + Zn$ $\Box$ (b) $Pb + Sb$ $\Box$	120.	Al <sub>4</sub> C <sub>3</sub> on hydrolysis gives gas.
	(c) $Cu + Sn$ $\Box$ (d) $Pb + Sn$ $\Box$		[J.E.E. (Orissa) 2007]
109.	For making good quality mirrors, plates of float glass are		(a) $CH_4$ $\Box$ (b) $C_2H_6$ $\Box$
102.	used. These are obtained by floating molten glass over a	101	(c) $C_2H_4$ $\Box$ (d) $C_2H_2$ $\Box$
	liquid metal, which does not solidify before the glass. The	121.	Diamond is hard because: [V.I.T.E.E.E. 2008]
	metal used is: [A.I.E.E.E. 2003]		(a) all the four valence electrons are bonded to each carbon
	(a) Hg		atoms by covalent bonds
	(c) Na $\Box$ (d) Mg $\Box$		(b) it is a giant molecule
110.	'A' when added to silica will give 'B'. 'A' and 'B' are:		(c) it is made up of carbon atoms $\Box$
1100	[D.P.M.T. 2007]		(d) it cannot be burnt
	(a) $HF, H_2SiF_4$ $\Box$ (b) $HF, H_2SiF_6$ $\Box$	122.	Among the following substituted silanes the one which will
	(c) $HCl_1H_2SiCl_6$ $\Box$ (d) $HI_1H_2SiL_6$ $\Box$		give rise to cross-linked silicone polymer on hydrolysis is:
111.	In $SiF_6^2$ and $SiCl_6^2$ which one is known and why?		[A.I.E.E.E. 2008]
111.			(a) $R_3$ SiCl $\Box$ (b) $R_4$ Si $\Box$
	[D.C.E. (Engg.) 2007]		(c) $RSiCl_3$ $\square$ (d) $R_2SiCl_2$ $\square$
	(a) $SiF_6^2$ because of small size of F	123.	The incorrect statement/s among the following is/are:
	(b) $SiF_6^{2-}$ because of large size of F		[P.E.T. (Kerala) 2008]
	(c) $SiCl_6^{2-}$ because of small size of Cl		I. NCl <sub>5</sub> does not exist while PCl <sub>5</sub> does.
	(d) $SiCl_6^{2-}$ because of large size of Cl		II. Lead prefers to form tetravalent compounds.

	III. The three C—O bonds are not equal in the carbonate		(c) hydrolysis of (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> followed by condensatio	n —
	ion.		polymerisation	
	IV. Both O <sub>2</sub> <sup>+</sup> and NO are paramagnetic.		(d) hydrolysis of (CH <sub>3</sub> ) <sub>3</sub> SiCl followed by condensation	n
	(a) I, III and IV $\Box$ (b) I and IV $\Box$		polymerisation [	
	(c) II and III	128.	Which of the following statements is not correct?	
	(e) ·IV only □		[J.E.E. (W.B.) 2009	9]
	[Hint: Lead prefers to form divalent compounds due to inert pair		(a) Silicon is used extensively as a semiconductor	
	effect. In carbonate ion, all the three C—O bonds are equal		· · · · · · · · · · · · · · · · · · ·	
	due to resonance.]		· ·	
124.	In silica, SiO <sub>2</sub> , each silicon atom is bonded to:		, -	
	[U.P.S.E.E. (Engg.) 2008]	129.	On heating K <sub>4</sub> Fe(CN) <sub>6</sub> with Conc. H <sub>2</sub> SO <sub>4</sub> gives the gas:	
	(a) two oxygen atoms $\Box$	1	[J.E.E. (Orissa) 2009	
	(b) four oxygen atoms			
•	(c) one silicon and two oxygen atoms			
	(d) one silicon and four oxygen atoms $\Box$	130	Products formed, when Pb(NO <sub>3</sub> ) <sub>2</sub> is heated, are:	LI
125.	C—C bond length is maximum in: [U.P.S.E.E. (Engg.) 2008]	150.	[J.E.E. (Orissa) 2009	61
	(a) diamond			
	(c) naphthalene $\square$ (d) fullerene $\square$			
126.	and financial section of the contract of the c	121	(c) PbO, $NO_2$ , $O_2$ $\square$ (d) Pb, $N_2$ , $O_2$ $\square$	
	liberated? [C.P.M.T. 2008]	131.	The products of the following reaction are:	
	(a) CO $\Box$ (b) O <sub>2</sub> $\Box$		$SiO_2 + C \xrightarrow{Heat} Products$	
	(c) $CO_2$ $\Box$ (d) $O_3$ $\Box$		[J.E.E. (Orissa) 2010	0]
127.	The straight chain polymer is formed:		2	
	[C.B.S.E. (P.M.T.) 2009]		(c) SiC and CO	
	(a) hydrolysis of CH <sub>3</sub> SiCl <sub>3</sub> followed by condensation poly-	132.	Which of the following has least tendency to undergo	go
	merisation		catenation ? [A.M.U. (Engg.) 201	0]
	(b) hydrolysis of (CH <sub>3</sub> ) <sub>4</sub> Si followed by addition poly-		(a) C	
	(b) hydrorysis or (Crrs/401 followed by addition pory-	1		_
_			(c) Ge $\square$ (d) Sn	
,	merisation $\Box$		(c) Ge	L
Set ]	merisation $\square$	orrect a		Ц
	merisation   This set contains questions with two or more co	orrect a	nswers.	
Set 1	merisation   This set contains questions with two or more contained is isostructural with:	orrect a	nswers.  (c) C <sub>3</sub> O <sub>2</sub> is also toxic like CO	
	merisation   This set contains questions with two or more contains dioxide is isostructural with:  (a) HgCl <sub>2</sub>		nswers.  (c) C <sub>3</sub> O <sub>2</sub> is also toxic like CO (d) Zircon, ZrSiO <sub>4</sub> is a gemstone	
133.	merisation $\square$ II : This set contains questions with two or more contains dioxide is isostructural with:  (a) $HgCl_2$ $\square$ (b) $SnCl_2$ $\square$ (c) $C_2H_2$ $\square$ (d) $NO_2$ $\square$	139.	(c) C <sub>3</sub> O <sub>2</sub> is also toxic like CO (d) Zircon, ZrSiO <sub>4</sub> is a gemstone The non-existence of PbI <sub>4</sub> is due to:	
	merisation $\square$ II: This set contains questions with two or more contains discrete contains questions with two or more contains discrete contains questions with two or more contains and discrete contains $\square$ (a) $\square$ (b) $\square$ (c) $\square$ (b) $\square$ (c) $\square$ (c) $\square$ (d) $\square$ (d) $\square$ (e) $\square$ (e) $\square$ (d) $\square$ (e) $\square$ (full times of the contains an arrange of the contains an arrange of the contains an arrange of the contains an arrange of the contains an arrange of the contains an arrange of the contains an arrange of the contains an arrange of the contains and the contains are contains an arrange of the contains and the contains are contains an arrange of the contains are contains an arrange of the contains are contains an arrange of the contains are contains an arrange of the contains are contains an arrange of the contains are contains an arrange of the contains are contains an arrange of the contains are contained as a contains a co		(c) C <sub>3</sub> O <sub>2</sub> is also toxic like CO (d) Zircon, ZrSiO <sub>4</sub> is a gemstone The non-existence of PbI <sub>4</sub> is due to: (a) highly oxidising nature of Pb <sup>4+</sup>	_ _ _
133.	merisation $\square$ II: This set contains questions with two or more contains discrete contains questions with two or more contains discrete contains questions with two or more contains and the contains $\square$ (a) $\square$ (b) $\square$ (b) $\square$ (c) $\square$ (c) $\square$ (d) $\square$ (e) $\square$ (e) $\square$ (e) $\square$ (for all $\square$ (f		(c) C <sub>3</sub> O <sub>2</sub> is also toxic like CO (d) Zircon, ZrSiO <sub>4</sub> is a gemstone The non-existence of PbI <sub>4</sub> is due to: (a) highly oxidising nature of Pb <sup>4+</sup> (b) highly reducing nature of Pb <sup>4+</sup>	
133. 134.	merisation $\square$ Carbon dioxide is isostructural with:  (a) $\operatorname{HgCl}_2$ $\square$ (b) $\operatorname{SnCl}_2$ $\square$ (c) $\operatorname{C}_2\operatorname{H}_2$ $\square$ (d) $\operatorname{NO}_2$ $\square$ CO is isostructural with:  (a) $\operatorname{SnCl}_2$ $\square$ (b) $\operatorname{HgCl}_2$ $\square$ (c) $\operatorname{SnCl}_2$ $\square$ (d) $\operatorname{HgCl}_2$ $\square$ (e) $\operatorname{SnCl}_2$ $\square$ (f) $\operatorname{HgCl}_2$ $\square$ (f) $\operatorname{SnCl}_2$ $\square$ (g) $\operatorname{HgCl}_2$ $\square$ (g) $\operatorname{SnCl}_2$ $\square$ (g) $\operatorname{HgCl}_2$ $\square$		(c) C <sub>3</sub> O <sub>2</sub> is also toxic like CO (d) Zircon, ZrSiO <sub>4</sub> is a gemstone  The non-existence of PbI <sub>4</sub> is due to: (a) highly oxidising nature of Pb <sup>4+</sup> (b) highly reducing nature of Pb <sup>4+</sup> (c) sufficiently large covalent character	
133. 134.	merisation $\square$ This set contains questions with two or more contains dioxide is isostructural with:  (a) $\operatorname{HgCl}_2$ $\square$ (b) $\operatorname{SnCl}_2$ $\square$ (c) $\operatorname{C}_2\operatorname{H}_2$ $\square$ (d) $\operatorname{NO}_2$ $\square$ CO is isostructural with:  (a) $\operatorname{SnCl}_2$ $\square$ (b) $\operatorname{HgCl}_2$ $\square$ (c) $\operatorname{SCl}_2$ $\square$ (d) $\operatorname{ZnI}_2$ $\square$ Which of the given is/are amphoteric?	139.	(c) $C_3O_2$ is also toxic like CO (d) Zircon, $ZrSiO_4$ is a gemstone  The non-existence of $PbI_4$ is due to: (a) highly oxidising nature of $Pb^{4+}$ (b) highly reducing nature of $Pb^{4+}$ (c) sufficiently large covalent character (d) highly reducing nature of $I^-$ ions	
133. 134.	merisation  II: This set contains questions with two or more contains divide is isostructural with:  (a) HgCl <sub>2</sub>		(c) $C_3O_2$ is also toxic like CO (d) Zircon, $ZrSiO_4$ is a gemstone  The non-existence of $PbI_4$ is due to: (a) highly oxidising nature of $Pb^{4+}$ (b) highly reducing nature of $Pb^{4+}$ (c) sufficiently large covalent character (d) highly reducing nature of $I^-$ ions  Which is not correct?	
133. 134.	merisation  II: This set contains questions with two or more contains discrete the contains questions with two or more contains discrete the contains questions with two or more contains questions	139.	(c) C <sub>3</sub> O <sub>2</sub> is also toxic like CO (d) Zircon, ZrSiO <sub>4</sub> is a gemstone The non-existence of PbI <sub>4</sub> is due to: (a) highly oxidising nature of Pb <sup>4+</sup> (b) highly reducing nature of Pb <sup>4+</sup> (c) sufficiently large covalent character (d) highly reducing nature of I <sup>-</sup> ions Which is not correct? (a) Ge(OH) <sub>2</sub> is amphoteric	
<ul><li>133.</li><li>134.</li><li>135.</li></ul>	merisation $\square$ II: This set contains questions with two or more contains discrete contains questions with two or more contains discrete contains questions with two or more contains and the contains $\square$ Carbon dioxide is isostructural with:  (a) $\square$ $\square$ (b) $\square$ $\square$ $\square$ (c) $\square$ $\square$ $\square$ $\square$ $\square$ $\square$ $\square$ $\square$ $\square$ $\square$	139.	(c) C <sub>3</sub> O <sub>2</sub> is also toxic like CO (d) Zircon, ZrSiO <sub>4</sub> is a gemstone The non-existence of PbI <sub>4</sub> is due to: (a) highly oxidising nature of Pb <sup>4+</sup> (b) highly reducing nature of Pb <sup>4+</sup> (c) sufficiently large covalent character (d) highly reducing nature of I <sup>-</sup> ions Which is not correct? (a) Ge(OH) <sub>2</sub> is amphoteric (b) SnCl <sub>4</sub> is more stable than SnCl <sub>2</sub>	
133. 134.	merisation $\square$ This set contains questions with two or more concarbon dioxide is isostructural with:  (a) $\operatorname{HgCl_2} \qquad \square \qquad \text{(b) SnCl_2} \qquad \square \qquad \text{(c) C_2H_2} \qquad \square \qquad \text{(d) NO_2} \qquad \square \qquad \text{CO is isostructural with:} \qquad \qquad \text{[I.I.T. (S) 1992]}$ (a) $\operatorname{SnCl_2} \qquad \square \qquad \text{(b) HgCl_2} \qquad \square \qquad \text{(c) SCl_2} \qquad \square \qquad \text{(d) ZnI_2} \qquad \square \qquad \text{Which of the given is/are amphoteric?}$ Which of the given is/are amphoteric?  [I.S.M.(Dhanbad) 1994]  (a) $\operatorname{BeO} \qquad \square \qquad \text{(b) Ag_2O} \qquad \square \qquad \text{(c) CO_2} \qquad \square \qquad \text{(d) SnO_2} \qquad \square \qquad \text{Decomposition of oxalic acid in presence of conc. H_2SO_4}$	139.	(c) C <sub>3</sub> O <sub>2</sub> is also toxic like CO (d) Zircon, ZrSiO <sub>4</sub> is a gemstone  The non-existence of PbI <sub>4</sub> is due to: (a) highly oxidising nature of Pb <sup>4+</sup> (b) highly reducing nature of Pb <sup>4+</sup> (c) sufficiently large covalent character (d) highly reducing nature of I <sup>-</sup> ions  Which is not correct? (a) Ge(OH) <sub>2</sub> is amphoteric (b) SnCl <sub>4</sub> is more stable than SnCl <sub>2</sub> (c) Trisilylamine is pyramidal	
<ul><li>133.</li><li>134.</li><li>135.</li></ul>	merisation  II: This set contains questions with two or more concepts of the contains questions with two or more concepts of the contains questions with two or more concepts of the contains questions with two or more concepts of the contains questions with two or more concepts of the contains questions with two or more concepts of the contains questions with two or more concepts of the contains questions with two or more concepts of the contains questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with two or more concepts questions with:  (a) HgCl <sub>2</sub>	139.	(c) $C_3O_2$ is also toxic like CO (d) Zircon, $ZrSiO_4$ is a gemstone  The non-existence of $PbI_4$ is due to: (a) highly oxidising nature of $Pb^{4+}$ (b) highly reducing nature of $Pb^{4+}$ (c) sufficiently large covalent character (d) highly reducing nature of $I^-$ ions  Which is not correct? (a) $Ge(OH)_2$ is amphoteric (b) $SnCl_4$ is more stable than $SnCl_2$ (c) Trisilylamine is pyramidal (d) $GeCl_4$ in $HCl$ forms $H_2[GeCl_6]$	
<ul><li>133.</li><li>134.</li><li>135.</li></ul>	merisation  II: This set contains questions with two or more concentrations dioxide is isostructural with:  (a) HgCl <sub>2</sub>	139.	(c) C <sub>3</sub> O <sub>2</sub> is also toxic like CO (d) Zircon, ZrSiO <sub>4</sub> is a gemstone  The non-existence of PbI <sub>4</sub> is due to: (a) highly oxidising nature of Pb <sup>4+</sup> (b) highly reducing nature of Pb <sup>4+</sup> (c) sufficiently large covalent character (d) highly reducing nature of I <sup>-</sup> ions  Which is not correct? (a) Ge(OH) <sub>2</sub> is amphoteric (b) SnCl <sub>4</sub> is more stable than SnCl <sub>2</sub> (c) Trisilylamine is pyramidal (d) GeCl <sub>4</sub> in HCl forms H <sub>2</sub> [GeCl <sub>6</sub> ]  Carbon differs from the rest of the family members becau	
<ul><li>133.</li><li>134.</li><li>135.</li><li>136.</li></ul>	merisation  II: This set contains questions with two or more concarbon dioxide is isostructural with:  (a) HgCl <sub>2</sub>	139.	(c) C <sub>3</sub> O <sub>2</sub> is also toxic like CO (d) Zircon, ZrSiO <sub>4</sub> is a gemstone The non-existence of PbI <sub>4</sub> is due to: (a) highly oxidising nature of Pb <sup>4+</sup> (b) highly reducing nature of Pb <sup>4+</sup> (c) sufficiently large covalent character (d) highly reducing nature of I <sup>-</sup> ions Which is not correct? (a) Ge(OH) <sub>2</sub> is amphoteric (b) SnCl <sub>4</sub> is more stable than SnCl <sub>2</sub> (c) Trisilylamine is pyramidal (d) GeCl <sub>4</sub> in HCl forms H <sub>2</sub> [GeCl <sub>6</sub> ] Carbon differs from the rest of the family members becausof:	
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<ul><li>133.</li><li>134.</li><li>135.</li><li>136.</li><li>137.</li></ul>	merisation ☐  II: This set contains questions with two or more concentrations dioxide is isostructural with:  (a) HgCl₂ ☐ (b) SnCl₂ ☐ (c) C₂H₂ ☐ (d) NO₂ ☐ CO is isostructural with:  (a) SnCl₂ ☐ (b) HgCl₂ ☐ (c) SCl₂ ☐ (d) ZnI₂ ☐ Which of the given is/are amphoteric?    I.S.M.(Dhanbad) 1994]  (a) BeO ☐ (b) Ag₂O ☐ (c) CO₂ ☐ (d) SnO₂ ☐ Decomposition of oxalic acid in presence of conc. H₂SO₄ gives:  (a) CO ☐ (b) CO₂ ☐ (c) formic acid ☐ (d) H₂O ☐ Which of the following are true about silicones?  (a) They are formed by hydrolysis of R₂ SiCl₂ ☐ (b) They are made up of SiO₄⁴ units ☐ (d) They are macromolecules ☐ Which among the following statements are correct?	139. 140.	(c) $C_3O_2$ is also toxic like CO  (d) Zircon, $ZrSiO_4$ is a gemstone  The non-existence of $PbI_4$ is due to:  (a) highly oxidising nature of $Pb^{4+}$ (b) highly reducing nature of $Pb^{4+}$ (c) sufficiently large covalent character  (d) highly reducing nature of $I^-$ ions  Which is not correct?  (a) $Ge(OH)_2$ is amphoteric  (b) $SnCl_4$ is more stable than $SnCl_2$ (c) Trisilylamine is pyramidal  (d) $GeCl_4$ in $HCl$ forms $H_2[GeCl_6]$ Carbon differs from the rest of the family members becautof:  (a) number of unpaired electrons in valence shell  (b) small size  (c) non-availability of vacant orbitals in valence shell  (d) non-availability of d-orbitals in valence shell  Which of the following carbides on treatment with war give methane?  [B.H.U. 200]  (a) $CaC_2$ [b) $Be_2C$	ase and attention of the control of

143.	Which of the metal oxide	es are	e reduced by CO?	144.	Which of the followi	ng are tl	ne ores of lead?	[B.H.U. 2007]
	(a) ZnO		(b) $Fe_2O_3$		(a) Galena		(b) Anglesite	
	(c) CaO		(d) Na <sub>2</sub> O		(c) Cerussite		(d) Plumbago	

H	nsw	ers						1		-					-				
1.	(a)	2.	(b)	3.	(c)	4.	(d)	5.	(a)	6.	(d)	7.	(b)	8.	(d)	9.	(b)	10.	(a)
11.	(b)	12.	(a)	13.	(b)	14.	(c)	15.	(d)	16.	(a)	17.	(b)	18.	(c)	19.	(a)	20.	(b)
21.	(c)	22.	(c)	23.	(c)	24.	(d)	25.	(d)	26.	(a)	27.	(d)	28.	(b)	29.	(d)	30.	(b)
31.	(a)	32.	(d)	33.	(a)	34.	(c)	35.	(c)	36.	(d)	37.	(c)	38.	(d)	39.	(b)	40.	(d)
41.	(d)	42.	(a)	43.	(b)	44.	(a)	45.	(c)	46.	(a)	47.	(c)	48.	(d)	49.	(a)	50.	(c)
51.	(b)	52.	(d)	53.	(c)	54.	(a)	55.	(b)	56.	(d)	<i>5</i> 7.	(b)	58.	(c)	59.	(d) ·	60.	(d)
61.	(a)	62.	(d)	63.	(b)	64.	(d)	65.	(c)	66.	(c)	67.	(a)	68.	(b)	69.	(a)	70.	(a)
71.	(c)	72.	(b)	73.	(b)	74.	(d)	75.	(b)	76.	(c)	77.	(b)	78.	(c)	79.	(b)	80.	(a)
81.	(a) -	82.	(c)	83.	(a)	84.	(d)	85.	(d)	86.	(b)	87.	(c)	88.	(b)	89.	(a)	90.	(c)
91.	(b)	92.	(a)	93.	(c)	94.	(d)	95.	(d)	96.	(d)	97.	(a)	98.	(a)	99.	(d)	100.	(d)
101.	(b)	102.	(a)	103.	(d)	104.	(d)	105.	(d)	106.	(c)	107.	(b)	108.	(d)	109.	(a)	110.	(b)
111.	(a)	112.	(d)	113.	(d)	114.	(a)	115.	(b)	116.	(a)	117.	(d)	118.	(a)	119.	(b)	120.	(a)
121.	(a)	122.	(c)	123.	(c)	124.	(b)	125.	(a)	126.	(c)	127.	(c)	128.	(c)	129.	(c)	130.	(c)
131.	(c)	132.	(d)	133.	(a, c)	134.	(b, d)	135.	(a, d)	136.	(a,b,d)	137.	(a, b, d)	138.	(a, b, d)	139.	(a, d)	140.	(b,c)
141.	(b, d)	142.	(b,c)	143.	(a, b)	144.	(a,b,c)												

#### **Objective Questions for IIT ASPIRANTS**



- 1. A red coloured mixed oxide (X) on treatment with conc. HNO<sub>3</sub> gives a compound (Y). (Y) with HCl produces a chloride (Z)which is insoluble in cold water but soluble in hot water.(Z) can also be formed by treating (X) with conc. HCl. Compounds (X), (Y) and (Z) are:
  - (a) Pb<sub>3</sub>O<sub>4</sub>, PbO<sub>2</sub>, PbCl<sub>2</sub>
- (b) Mn<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub>, MnCl<sub>2</sub>
- (c) Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, FeCl<sub>3</sub>
- (d) Fe<sub>3</sub>O<sub>4</sub>, FeO, FeCl<sub>2</sub>

[Hint:  $Pb_3O_4(X)$  is red coloured mixed oxide consisting PbO and

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb (NO_3)_2 + PbO_2 + 2H_2O;$$

$$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$$

PbCl<sub>2</sub> is insoluble in cold water but soluble in hot water.  $Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$ 

- 2. An inorganic compound (A) made of two most occurring elements in the earth's crust and used in building construction when made to react with carbon, forms a poisonous gas (B) which is most stable diatomic molecule. Compounds (A) and (B) are:
  - (a) SiO<sub>2</sub>, CO<sub>2</sub>
- (b) SiO<sub>2</sub>, CO
- (c)  $SiO_2$ ,  $N_2$
- (d) CaO, CO<sub>2</sub>

[Hint: SiO<sub>2</sub> is a compound of oxygen and silicon, the two most abundant elements of earth's crust and is used in building

> $SiO_2 + 2C \longrightarrow Si + 2CO$  (poisonous gas and a stable diatomic molecule) ]

 $\operatorname{SnCl}_2 + \operatorname{HCl} + \operatorname{I}_2 \longrightarrow (A) + (B)$ 

The compounds (A) and (B) are:

- (a)  $SnI_2$ ,  $Cl_2$
- (b) H<sub>2</sub>SnCl<sub>4</sub>, HI
- (c) SnCl<sub>4</sub>, HI
- (d) HSnCl<sub>3</sub>, HI

[Hint: SnCl2 decolourises iodine forming colourless HI.

$$SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI$$

- 4. Bucky ball or buckminsterfullerene:
  - (a) is an allotrope of carbon
  - (b) is referred as C-60
  - (c) has  $sp^2$  hybridized nature and resembles with soccer ball
  - (d) all of the above
- When concentrated H<sub>2</sub>SO<sub>4</sub> is added to K<sub>4</sub>Fe(CN)<sub>6</sub>, CO is evolved. If in place of concentrated H<sub>2</sub>SO<sub>4</sub>, dilute H<sub>2</sub>SO<sub>4</sub> is used, what gas will be evolved?
  - (a) CO

(b) HCN

(d) CO<sub>2</sub>

[Hint:  $K_4Fe(CN)_6 + 3H_2SO_4$  (dil.)  $\rightarrow 2K_2SO_4 + FeSO_4 + 6HCN$ ]

- Which tetrahalide does not act as Lewis acid?
  - (a) CCl<sub>4</sub>

- (b) SiF<sub>4</sub>
- (c) GeCl<sub>4</sub>
- (d) SnCl<sub>4</sub>

[Hint: CCl<sub>4</sub> does not form hexachloro complex as d-orbitals are not present in carbon but rest of the tetrahalides can form hexahalo complexes.]

- 7. A mixture of two gases is formed when an organic acid is heated with conc. H<sub>2</sub>SO<sub>4</sub>. When the gaseous mixture is passed through KOH solution, one gas is absorbed. The unabsorbed gas combines with chlorine and forms a poisonous gas. The organic acid and the two gases evolved with conc.  $H_2SO_4$  are respectively:
  - (a) CH<sub>3</sub>COOH, CO<sub>2</sub>, CO
- .(b) oxalic acid, CO<sub>2</sub>, CO
- (c) HCOOH, CO, H2O
- (d) none of these

[Hint: COOH]
$$\begin{array}{c} \text{Conc.H}_2\text{SO}_4 \\ \text{COOH} \end{array} \xrightarrow{\text{Conc.H}_2\text{SO}_4} \text{CO} + \text{CO}_2 \xrightarrow{\text{KOH}} \text{CO}_2 \text{ is absorbed COCl}_2 \end{array}$$

- 8.  $2 RCl + Si \xrightarrow{Cu \text{ powder}} R_2 SiCl_2 \xrightarrow{H_2O} R_2 Si(OH)_2 \xrightarrow{Polymerisation}$ 
  - (A), (A) is:
  - (a) cyclic silicone
- (b) cross linked silicone
- (c) linear silicone
- (d) none of these

[Hint: See page no. 426]

- 9.  $SiCl_4 \xrightarrow{H_2O} (A) \xrightarrow{Heat} (B) \xrightarrow{+Na_2CO_3}$ (C). The compound (C) is:
  - (a) SiO<sub>2</sub>
- (b) Si
- (c) SiC

$$[\textbf{Hint}: SiCl_4 + H_2O \longrightarrow Si(OH)_4 \xrightarrow{\quad Heat \quad} SiO_2 \xrightarrow{\quad Na_2CO_3 \quad } Heat \quad \\ (A) \qquad \qquad (B)$$

Na<sub>2</sub>SiO<sub>3</sub>]

- 10. When a mixture of air and steam is passed over red hot coke, the outgoing gas contains:
  - (a) producer gas
- (b) water gas
- (c) coal gas
- (d) mixture of (a) and (b)

[Hint: Coke + air  $\longrightarrow$  CO + N<sub>2</sub>; Coke + H<sub>2</sub>O  $\longrightarrow$  CO+H<sub>2</sub>] Steam

- Producer gas
- 11. Lead oxide (PbO) can be dissolved in:
  - (a) HNO<sub>3</sub>
- (c) H<sub>2</sub>SO<sub>4</sub>
- (d) H<sub>2</sub>O

[Hint: PbO dissolves in HNO3 as it forms lead nitrate which is soluble.

$$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$$

HCl forms insoluble PbCl2 and H2SO4 forms insoluble PbSO<sub>4</sub>. PbO is insoluble in water also.]

- 12. Which silicon compound is used as lubricant?
  - (a) Asbestos
- (b) Silicone
- (c) Zeolite
- (d) Mica
- 13. A colourless solution (X) gives black precipitate on passing  $H_2S$ . (X) also gives a white precipitate with stannous chloride which gradually changes to grey. What may be (X)?
  - (a) PbCl<sub>2</sub>
- (b) CdBr<sub>2</sub>
- (c) HgCl<sub>2</sub>
- (d)  $Cu(NO_3)_2$

[Hint:  $HgCl_2 + H_2S \longrightarrow HgS + 2HCl$ ;

 $\begin{array}{ccc} HgCl_2 + SnCl_2 & \longrightarrow & Hg_2Cl_2 & \xrightarrow{SnCl_2} & 2Hg \end{array}]$   $\begin{array}{ccc} White & \longrightarrow & Grev \end{array}$ 

14. 
$$CaCO_3(s) \xrightarrow{Heat} (A)(s) + (B)(g)$$

$$+ Carbon \\ heat \\ (C)(s) + (D)(g)$$

$$(C)(s) + H_2O \longrightarrow (E)(g).$$
The compound  $(E)(g)$  is:

(a)  $CO$ 
(b)  $CO_2$ 
(c)  $CH_4$ 
(d)  $C_2H_2$ 

[Hint: 
$$CaCO_3 \xrightarrow{Heat} CaO + CO_2$$

$$(A) \qquad (B)$$

$$CaO + C \xrightarrow{Heat} CaC_2 + CO$$

$$(C) \qquad (D)$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2 ]$$

$$(E)$$

- 15. A white coloured inorganic salt gives the following reactions:
  - (i) It is soluble in water and the solution has sweet taste. The solution turns black in presence of  $H_2S$ .
  - (ii) The salt when heated gives acetone and a yellow coloured residue which is used in paints.
  - (iii) The solution of the salt gives a white precipitate with dilute HCl which is soluble in hot water.

    The inorganic salt is:
  - (a) Ca (CH<sub>3</sub>COO)<sub>2</sub>
- (b) Zn (CH<sub>3</sub>COO)<sub>2</sub>
- (c) Pb (CH<sub>3</sub>COO)<sub>2</sub>
- (d) Ba(CH<sub>3</sub>COO)<sub>2</sub>

- [Hint: The solution of lead acetate is sweet in taste, when HCl is added to its solution, it forms PbCl<sub>2</sub> which is soluble in hot water.
  - Lead acetate on heating gives acetone and lead oxide (yellow residue).

$$Pb(CH_3COO)_2 \longrightarrow CH_3COCH_3 + PbO + CO_2$$
]

- 16. Which of the following bonds is the weakest?
  - (a) Si-Si
- (b) Si--O
- (c) Si-Cl
- (d) Si—H
- 17. Which metal does not form nitrate when heated with conc. HNO<sub>3</sub>?
  - (a) Zn

(b) Mg

(c) Sn

(d) Pb

[Hint:  $Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$ ]

- **18.** Germanium (II) compounds are powerful reducing agents whereas lead (IV) compounds are strong oxidising agents. It is due to:
  - (a) Pb is more electronegative than Ge.
  - (b) the ionisation energy of Pb is less than that of Ge.
  - (c) the ionic radii of Pb<sup>2+</sup> and Pb<sup>4+</sup> are less than those of Ge<sup>2+</sup> and Ge<sup>4+</sup>.
  - (d) more pronounced inert pair effect in Pb than in Ge.

[Hint: Inert pair effect increases in IVth group as the atomic number increases, *i.e.*, the stability of divalent state increases from Ge<sup>2+</sup> to Pb<sup>2+</sup>.]

#### 1. (a) 2. (b) 3. (c) 4. (d) 5. (b) **6.** (a) 7. (b) 8. (c) 9. (d) 10. (d) **11.** (a) 12. (b) 18. (d) 13. (c) 14. (d) 15. (c) 16. (a) 17: (c)

# **Assertion-Reason Type Questions**

In each of the following questions two statements are given as **Assertion** (A) and **Reason** (R). Examine the statements and answer the questions according to the instructions given below:

Mark (a) if both (A) and (R) are correct and (R) is the correct explanation of (A).

Mark (b) if both (A) and (R) are correct but (R) is not the correct explanation of (A).

Mark (c) if (A) is correct but (R) is wrong.

Mark (d) if (A) is wrong but (R) is correct.

Mark (e) if both (A) but (R) are wrong.

- 1. (A) Graphite is a good conductor of heat and electricity.
  - (R) Free electrons are spread out in the structure of graphite.
- 2. (A) Carbon dioxide is a poisonous gas.
  - (R) Carbon dioxide combines with haemoglobin of blood to form carboxyhaemoglobin which is not capable of absorbing oxygen.
- 3. (A) + 4 oxidation state of Pb is less stable than +2 state.
  - (R) PbI<sub>4</sub> is not a stable compound.

- **4.** (A) Carbon forms a large number of compounds.
  - (R) Carbon is found in abundance in nature.
- 5. (A) Both CO<sub>2</sub> and SiO<sub>2</sub> have same structure.
  - (R) CO<sub>2</sub> is a gas while SiO<sub>2</sub> is a crystalline compound.
- 6. (A) Carborundum is used as an abrasive.
  - (R) Its structure is similar to diamond.
- 7. (A) Maximum covalency of carbon is four.
  - (R) Carbon has no d-orbitals in valence shell.
- 8. (A) Lead leaves a black mark on paper.
  - (R) Lead is used for making lead pencils.
- **9.** (A)  $SiF_6^{2-}$  is known but  $SiCl_6^{2-}$  is not.
  - (R) Size of fluorine is small and its lone pair of electrons interacts with d-orbitals of silicon strongly.
- **10.** (A) Silicones are hydrophobic in nature.
  - (R) Si—O—Si linkages are moisture sensitive.
- 11. (A) CO<sub>2</sub> is linear.
  - (R) It is not in sp hybridized state.

[E.A.M.C.E.T. (Med.) 2007]

- 12. (A) Pb<sup>4+</sup> compounds are stronger oxidising agents than Sn<sup>4+</sup> compounds.
  - (R) The higher oxidation states for the group 14 are more stable for the heavier members of the group due to inert pair effect. [I.I.T. 2008]
- 13. (A) Graphite is soft while diamond is very hard.
  - (R) Graphite has three dimensional structure while diamond has planar. [B.H.U. 2008]
- 14. (A) Silica is soluble in HF.
  - (R)  $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$  $SiF_4 + 2HF \longrightarrow H_2SiF_6$

[B.H.U. 2008]

Ansu	vers	* * * * * * * * * * * * * * * * * * * *		· ·					
1. (a)	<b>2.</b> (e)	<b>3.</b> (b)	<b>4.</b> (c)	<b>5.</b> (d)	<b>6.</b> (b)	7. (a)	<b>8.</b> (c)	<b>9.</b> (a)	10. (c)
<b>11.</b> (c)	<b>12.</b> (c)	<b>13.</b> (c)	<b>14.</b> (a)		,				

# THOUGHT TYPE QUESTIONS

#### THOUGHT 1

When a mixture of sodium carbonate and calcium carbonate is fused with silica at 1500°C, a liquid consisting silicates of sodium and calcium is formed. When this liquid is cooled, it becomes viscous and eventually ceases to flow. It becomes solid and called glass. By varying the proportions of the three basic ingredients and by adding other substances, the properties of glass can be altered. An approximate formula for ordinary glass may be given as,

gradustication — e colo decretal deservation de contrata de contra

#### $R_2O-MO-6SiO_2$

where R = Na or K and M = Ca, Ba, Zn and Pb.

SiO<sub>2</sub> may be replaced by Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>. Coloured glasses are obtained by adding certain metallic oxides or salts in the fused mass. Glass is attacked by HF and this property is used to make marking on the glass. This is known as etching.

The glass if cooled rapidly becomes brittle and fragile. The articles of glass are cooled neither very slowly nor very rapidly. The articles are cooled gradually. This process is termed annealing.

- 1. Glass is described as a:
  - (a) solid

- (b) liquid
- (c) super cooled liquid
- (d) colloidal solution
- 2. Which acid cannot be stored in glass?
  - (a) HF

(b) HCl

(c) HBr

(d) HI

[Hint: HF attacks glass. Na<sub>2</sub>SiO<sub>3</sub> + 6HF  $\longrightarrow$  Na<sub>2</sub>SiF<sub>6</sub> + 3H<sub>2</sub>O]

- 3. Ordinary glass is:
  - (a) sodium silicate
- (b) potassium silicate
- (c) calcium silicate
- (d) a mixture of sodium and calcium silicates with silica
- 4. Annealing is the best described as:
  - (a) slow and gradual cooling
  - (b) sudden and rapid cooling
  - (c) cooling by water
  - (d) very slow cooling
- 5. A blue colour can be imparted to glass by use of:
  - (a)  $Fe_2O_3$
- (b) CoO

(c) NiO

(d) Cu<sub>2</sub>O

- 6. A special type of glass which contains cerium oxide and does not allow the passage of ultraviolet rays. This glass is used for making lenses. The glass is called:
  - (a) flint glass
- (b) Crooke's glass
- (c) hard glass
- (d) pyrex glass

# THOUGHT 2

Gaseous fuels have become very popular these days. The following are the advantages of gaseous fuels.

- (i) They have high calorific value.
- (ii) They do not produce smoke and leave no ash after combustion.
- (iii) Gaseous fuels can flow through pipes and can be ignited at the moments notice at any place. No special devices are required for their combustion.

Coal gas is a good gaseous fuel as it contains 95% combustible gases such as hydrogen, methane, carbon monoxide, etc. It is obtained by destructive distillation of coal at about 1000°C. Water gas which is essentially a mixture of hydrogen and carbon monoxide is prepared by passing steam over incandescent coke. The reaction is however endothermic. Producer gas which possesses lowest calorific value is prepared by passing air over red hot coke. It contains mainly nitrogen and carbon monoxide. Semiwater gas is a mixture of water gas and producer gas. Oil gas which is used in laboratories is obtained by cracking of kerosene. It is a mixture of hydrocarbons (saturated and unsaturated) mainly lower hydrocarbons. LPG (liquefied petroleum gas), which contains C<sub>3</sub> and C<sub>4</sub> hydrocarbons of the alkane and alkene series supplied in cylinders for domestic uses is very popular these days.

- 1. Which one is the best fuel?
  - (a) Wood
- (b) Coal
- (c) Kerosene
- (d) LPG
- 2. Which gaseous fuel has the highest calorific value?
  - (a) Producer gas
- (b) Semiwater gas
- (c) Coal gas
- (d) Water gas
- **3.** Which of the following contains the highest percentage of carbon monoxide?

- (a) Coal gas
- (b) Water gas
- (c) Producer gas
- (d) Natural gas
- 4. Which of the following is a cracking process?
  - (a)  $C_3H_6 + H_2 \longrightarrow C_3H_8$

  - (b)  $nC_2H_4 \longrightarrow (C_2H_4)_n$ (c)  $C_{16}H_{34} \longrightarrow 6CH_4 + 2C_2H_4 + C_2H_2 + 4C$
  - (d)  $3C_2H_2 \longrightarrow C_6H_6$
- Which gas is essential constituent of the most of fuel gases?
  - (a) CO

(b) CO<sub>2</sub>

(c) N<sub>2</sub>

(d) H<sub>2</sub>O

#### THOUGHT 3

The heavier elements of group 13, 14 and 15 besides their group oxidation state exhibit another oxidation state which is two units lower than the group oxidation state. The stability of lower oxidation state increases down the group.

The display of lower oxidation state is due to inert pair effect.

- 1. Which of the halide does not exist?
  - (a) TICl

- (b) PbBr<sub>4</sub>
- (c) PbCl<sub>2</sub>
- (d) SnCl<sub>2</sub>

- (d) In Tl + 1 oxidation state is more stable than +3 oxidation
  - 3. The strongest reducing agent among the following is:

(b) In Ga + 3 oxidation state is more stable than +1 oxidation

(c) In Sn + 2 oxidation state is more stable than +4 oxidation

2. Which of the following statements is incorrect?

(a) Boron shows only +3 oxidation state.

(a) GeCl<sub>2</sub>

state.

- (b) SnCl<sub>2</sub>
- (c) PbCl<sub>2</sub>
- (d) TICI
- 4. The strongest oxidising agent among the following is:

(b) GeO2

(c) SnO<sub>2</sub>

- (d) PbO<sub>2</sub>
- 5. Inert pair effect is not exhibited by:
  - (a) Pb

(b) Bi

(c) Tl

- (d) B
- 6. Which of the following compounds do not undergo disproportionation in aqueous solution?
  - (a) TlCl<sub>3</sub>

(b) GaCl

(c) InCl

(d) TICI

4. (a) Thought 1 1. (c) 2. (a) 3. (d) 5. (b) 6. (b) Thought 2 1. (d) 2. (c) 3. (b) 4. (c) 5. (a) Thought 3 1. (b) 2. (c) 3. (a) 4. (d) 5. (d) 6. (a, d)

#### **BRAIN STORMING PROBLEMS**



- 1. Which among the following halides is coloured and why? CCl<sub>4</sub>, SiBr<sub>4</sub> and SnI<sub>4</sub>.
  - [Ans. SnI<sub>4</sub> yellow/orange solid]
- 2. Which crystalline allotropic form of carbon has the lowest energy?
  - [Ans. Graphite—It has  $3\sigma$  and  $\pi$ -bond whereas in diamond there are 4 $\sigma$ -bonds. Thus, graphite has low energy.]
- 3. What are the differences in following two classes of carbides? Class 1. Be<sub>2</sub>C, Al<sub>4</sub>C<sub>3</sub>
  - Class 2.  $CaC_2$ ,  $Al_2C_6$
  - [Ans. Class 1. Carbides are methanides because they evolve methane gas on hydrolysis.
    - Class 2. Carbides are called acetylides because they evolve acetylene on hydrolysis.]
- 4. What do you understand by semiwater gas?
  - [Ans. Mixture of producer and water gas is called semiwater gas.]
- 5. Explain the structure of C<sub>3</sub>O<sub>2</sub> in terms of bonding in the molecule.
  - [Ans. It is carbon suboxide with following linear structure,

$$0 = C = C = C = 0$$

Each carbon lies in sp hybrid state. The  $\pi$ -electrons are delocalized from one end to other. The delocalization does not alter the geometry of molecule.]

- **6.**  $\operatorname{Sn}^{2+}(aq.)$  may also be written as  $\left[\operatorname{Sn}(H_2O)_6\right]^{2+}$ , this ion is acidic by hydrolysis, write a possible equation for this hydrolysis.
- 7. Which among the following oxides of lead is strong oxidising agent?

- [Ans. PbO<sub>2</sub>—It oxidises HCl to Cl<sub>2</sub>]
- **8.** Which method is used to get semiconductor grade silicon? [Ans. Zone refining]
- **9.** What is peculiarity in electrical property of quartz?
  - Quartz crystals exhibit piezoelectric effect. Compression of the crystal in particular direction causes an electric voltage to develop across. Such crystals are used in phonograph; microphones to convert sound vibrations to alternating electric current. The opposite effect is also possible; the alternating current when applied to piezoelectric crystal can make it to vibrate.]
- 10. Which of the following oxides of carbon act as a reducing agent and why?

$$CO, CO_2, C_3O_2$$

[Ans. CO; there is lone pair of  $e^-$  at carbon to be denoted; hence carbon monoxide acts as reducing agent.]

11. Classify the following silicates:

(a) Beryl (b) Feldspar (c) Spodumene (d) Zircon [Ans. (a) Cyclic, (b) Three dimensional sheet, (c) Chain silicate, (d) Orthosilicate]

(u) Offilosificate

12. Explain why the silicate olivine (FeMg)<sub>2</sub>SiO<sub>4</sub> does not follow the law of constant composition.

[Ans. Any ratio of iron to magnesium may be found. It may be treated as solution of Fe<sub>2</sub>SiO<sub>4</sub> in Mg<sub>2</sub>SiO<sub>4</sub> and *vice-versa*.]

13. What are the following compounds? Give their uses:

(i) Vitrosil

(ii) Carbogen

(iii) Kieselguhr

(iv) Chrome yellow and chrome red

(v) Butter of tin

(vi) Litharge and Massicot

(vii) Carburated water gas

(viii) Crooke's glass

(ix) Opal glass

[Ans.

(i) Quartz glass used in the manufacture of optical instruments is called **vitrosil**.

(ii) Carbogen is a mixture of 95% O<sub>2</sub> and 5% CO<sub>2</sub>. It is used for artificial respiration for the victims of carbon monoxide poisoning.

(iii) Kieselguhr—It is a mass of hydrated silica (SiO<sub>2</sub>) formed from skeletons of minute plants known as diatoms. It is highly porous and absorbent material used in the manufacture of dynamite.

(iv) Chrome yellow (PbCrO<sub>4</sub>) is used as yellow pigment chrome red (PbCrO<sub>4</sub> PbO) is used as red pigment.

(v) SnCl<sub>4</sub>·5H<sub>2</sub>O is called butter of tin and is used as a mordant in dyeing.

(vi) Red form of PbO is called litharge and yellow form of PbO is called massicot.

(vii) Carburated water gas is a mixture of carbon monoxide (23-28%); H<sub>2</sub> (34-38%), saturated hydrocarbons (17-21 %),

unsaturated hydrocarbons (13–16%);  $CO_2$  (upto 2%) and  $(N_2$  upto 5%).

(viii) Crooke's glass is used in UV filter glasses. It contains CeO<sub>2</sub>.

(ix) Sometimes CaF<sub>2</sub> is added to obtain opal glass.]

**14.** Give the names of ions that produce deep blue, light blue, ruby red, green colour and yellow-brown colour in the glass.

[Ans. Colour
Deep blue
Light blue
Ruby red
Green colour
Yellow-brown

Metal ions

Co<sup>2+</sup>

Cu<sup>2+</sup>

Cu +/Cu<sup>2+</sup>

Mixture of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions

**15.** Give the molecular formula of talc and muscovite. Comment on their structure and use.

[Ans. Talc: Mg<sub>3</sub> Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>. It is one of the very soft material. It is used in talcum powder.

Muscovite: KAl<sub>2</sub> Si<sub>3</sub>AlO<sub>10</sub>(OH)<sub>2</sub>; it is a mica. It has layer type structure involving weak van der Waals' force.

16. Complete the following road map.

$$H_2C_2O_4 \xrightarrow{Conc. H_2SO_4} (A) + (B) + (C)$$
 $Gas Gas Liquid$ 

Gas (A) burns with blue flame and gas (B) turns lime water milky. Gas (A) on oxidation gives gas (B). Liquid (C) produces blue colour when comes in contact with anhydrous copper sulphate.

$$(A) + \operatorname{Cl}_2 \longrightarrow (D) \xrightarrow{\operatorname{NH}_3} (E)$$

$$(B) \xrightarrow{\operatorname{NH}_3} \Delta$$

What are the compounds (A) to (E)?

[Ans. (A) CO; (B) CO<sub>2</sub>; (C) H<sub>2</sub>O; (D) COCl<sub>2</sub>; (E) NH<sub>2</sub>CONH<sub>2</sub>]

# THURSANGAMES Type Duestions

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. The bond order of carbon monoxide is:
- 2. What is the value of x in the following silicate mineral?  $Be_3Al_2Si_xO_{18}$
- 3. The ratio of copper and tin in bell metal alloy is:
- **4.** Pb<sub>3</sub>O<sub>4</sub> is regarded as a compound oxide of PbO and PbO<sub>2</sub>. How many parts of PbO are present in it?
- 5. How many methanides are present in the following carbides? SiC, CaC<sub>2</sub>, Be<sub>2</sub>C, Al<sub>2</sub>C<sub>6</sub>, Al<sub>4</sub>C<sub>3</sub>, B<sub>4</sub>C
- **6.** Carbogen is a mixture of O<sub>2</sub> and CO<sub>2</sub>. It is used for artificial respiration. What is the percentage of CO<sub>2</sub> in this mixture?
- 7. In the giant structure of silica, each silicon atom is surrounded by how many oxygen atoms?

#### Auswers

1. (3)  $KK(\sigma 2s)^2 (\overset{*}{\sigma} 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2$ Bond order =  $\frac{10-4}{2}$  = 3

- **2.** (6)
- 3. (4) Cu 80% Sn 20% ratio = 80/20 = 4

- 4. (2) 2 parts PbO and 1 part PbO<sub>2</sub>.
- 5. (2) Be<sub>2</sub>C and Al<sub>4</sub>C<sub>3</sub> are methanides.
- 6. (5) 95% O<sub>2</sub> and 5% CO<sub>2</sub>.
- 7. (4) Each silicon atom is surrounded by four oxygen atoms tetrahedrally.

# Group VA or 15 7 N Nitrogen 25°22° 15 P Phosphorus 33°32° 33 AS Assenic 45°42° 51 Sb Antimony 55°52° 115 Uup Ununpentium 75°72°

# CHAPTER 10

# **Elements of Group VA or 15**

(Elements of Nitrogen and Phosphorus Family, ns<sup>2</sup>np<sup>3</sup>)

#### Contents:

10.1 Position in Periodic Table

10.2 Abnormal Behaviour of Nitrogen

**10.3** Nitrogen (N<sub>2</sub>)

10.4 Important Compounds of Nitrogen

10.5 Nitrates

10.6 Phosphorus

10.7 Compounds of Phosphorus

10.8 Arsenious Oxide or Arsenic Trioxide

10.9 Fertilizers

Group Period	IVA 14	VA 15	VIA 16
2	C (6)	N (7)	O (8)
3	Si (14)	P (15)	S (16)
4	Ge (32)	As (33)	Se (34)
5	Sn (50)	Sb (51)	Te (52)
6	Pb (82)	Bi (83)	Po (84)
7	Uuq (114)	Uup (115)	Uuh (116)

#### 10.1 POSITION IN PERIODIC TABLE

VA group or 15th group of the extended form of the periodic table consists of six elements—nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), bismuth (Bi) and ununpentium (Uup)\*. This group of six elements constitutes a family. These elements are collectively known as **pnictogens**. These are p-block elements as the last differentiating electron is accommodated on np shell. These elements have five electrons in the valency shell. The elements of the group possess the same electronic configuration and show similarities as well as gradation in their properties with rise of atomic number from nitrogen to ununpentium. Thus, their inclusion in the same group is justified on the basis of electronic configuration and physical and chemical properties which are given below:

**1. Electronic configuration**: The distribution of electrons in various energy shells of the atoms of these elements is given below:

Element	At. No.		Electronic configuration	Inert gas core
N	7	2, 5	$1s^2$ , $2s^2$ $2p^3$	[He] $2s^2 2p^3$
P	15	2, 8, 5	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^3$	[Ne] $3s^2 3p^3$
As	33	2, 8, 18, 5	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^3$	[Ar] $3d^{10}$ , $4s^2 4p^3$
Sb	51	2, 8, 18, 18, 5	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ , $5s^2$ $5p^3$	[Kr] $4d^{10}$ , $5s^2$ $5p^3$
Bi	83	2, 8, 18, 32, 18, 5	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ , $5s^2$ $5p^6$ $5d^{10}$ , $6s^2$ $6p^3$	[Xe] $4f^{14}$ , $5d^{10}$ , $6s^2$ $6p$
Uup	115	2, 8, 18, 32, 32, 18, 5	$5  ext{ } 1s^2, \ 2s^2 \ 2p^6, \ 3s^2 \ 3p^6 \ 3d^{10}, \ 4s^2 \ 4p^6 \ 4d^{10} \ 4f^{14}, \ 5s^2 \ 5p^6 \ 5d^{10} \ 5f^{14},$	[Rn] $5f^{14}$ , $6d^{10}$ , $7s^2$ $7p$
			$(6s^2 6p^6 6d^{10}, 7s^2 7p^3)$	

<sup>\*</sup>Ununpentium (115) has recently been discovered. It is a synthetic element. It is radioactive and is unstable in nature. Very little is known about its properties.

The configurations show that these elements have same number of electrons in the valency shell, *i.e.*, 5 electrons in the valency shell, two of which are in s-orbital and remaining three in three p-orbitals. Thus, they have  $ns^2 np^3$  configuration, *i.e.*, s-orbital is paired and three p-orbitals are unpaired.

The penultimate shell, in nitrogen contains 2 electrons (saturated), in phosphorus contains 8 electrons (saturated), in arsenic contains 18 electrons (saturated) while in antimony and bismuth contain 18 electrons (unsaturated) each. This shows why nitrogen differs from phosphorus in some respects and these two differ from the remaining elements of this group.

In accordance with the Hund's rule, electronic configurations involving fully filled or exactly half filled orbitals are the most stable, the elements of group VA, having exactly half filled orbitals, are also fairly stable and not so reactive. Nitrogen behaves as a **noble element** under ordinary conditions.

#### 2. Similarities and gradation in physical properties :

(a) Metallic and non-metallic character: Metallic nature increases as the atomic number increases. N and P are purely non-metals while Sb and Bi are metals. Arsenic behaves as a metalloid.

N and P combine with electropositive elements and form nitrides and phosphides, respectively. Nitrides are more stable than phosphides. Bi and Sb form alloys with other metals. Thus, N and P are non-metals while Sb and Bi are metals.

- (b) Physical state: There is a gradual change in physical state of these elements under ordinary conditions. Nitrogen, the first element, is a gas while phosphorus, the second member, though a solid, can pass readily into vapour state. It is soft waxy solid. The remaining elements are solids. These are hard and possess metallic lustre.
- (c) Atomic radii: The atomic radii of the elements of group 15 are smaller as compared to the elements of group 14 in the corresponding periods.

$$N < C$$
;  $P < Si$ ;  $As < Ge$  (70 pm) (77 pm) (110 pm) (118 pm) (121 pm) (122 pm)

This is due to increased effective nuclear charge which brings contraction in size.

Atomic radii increase on going down the group.

The increase is due to addition of a new energy shell in each succeeding element.

There is considerable increase in covalent radius from N to P but from As to Bi only a small increase is observed.

The considerable increase in covalent radius from N to P can be attributed to strong shielding effect of s- and p- electrons present in the inner shells. Small increase in covalent radii from As to Bi is, however, due to poor shielding effect of d- and/ or f-electrons present in the inner shells on valency electrons. This brings increase in effective nuclear charge which reduces the effect of the addition of a new energy shell to some extent.

(d) Ionisation energy or Ionisation enthalpy: The values of first ionisation energy are higher than the corresponding group 14 elements. However, the values gradually decrease on going down the group from nitrogen to bismuth.

On account of increased nuclear charge, reduced atomic radii and stable half filled configurations, it is more difficult to remove an electron as it is more tightly held by the nucleus. Subsequently, the values of ionisation energy of these elements are higher than the elements of group 14. The decrease in the values of ionisation energy from nitrogen to bismuth is due to gradual increase in atomic size.

The ionisation energy of nitrogen is very high; this is due to its small size. The difference between N and P is comparatively high but the difference afterwards between two consecutive members is small. This is due to less shielding effect of d-electrons in As and Sb, d and f-electrons in Bi.

Successive ionisation energies of these elements increase as expected, *i.e.*,  $E_1 < E_2 < E_3$ .

Element		N	P	As	Sb	Bi
Ionisation energy	$E_1$	1402	1012	947	834	703
(kJ mol <sup>-1</sup> )	$E_2$	2856	1903	1798	1595	1610
	$E_3$	4577	2910	2736	2443	2466

(e) Electronegativity: Electronegativity decreases gradually on descending the group from N to Bi.

Nitrogen is most electronegative element, i.e., typical non-metal

(f) Density: It increases gradually on descending the group.

Element N P As Sb Bi

Density (g/mL) 0.809 1.823 5.73 6.62 9.78

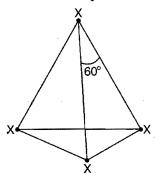
- (g) Allotropy: All the elements except bismuth show allotropy. Nitrogen exists in two solid allotropic forms,  $\alpha$ -nitrogen with cubic crystalline structure and  $\beta$ -nitrogen with hexagonal crystalline structure. The transition temperature is  $-238.5^{\circ}$ C. Phosphorus exists in number of allotropic forms such as white, red, scarlet,  $\alpha$ -black,  $\beta$ -black and violet. Arsenic is known in three allotropic forms, *i.e.*, grey, yellow and black. Antimony also exists in three forms, *i.e.*, yellow, black and explosive.
- (h) Catenation: N, P and As exhibit the property of catenation but this property is much less than IVA elements. No nitrogen compound containing nitrogen chain with more than two atoms is stable although compounds having a chain of eight nitrogen atoms have been prepared. The bond energies of C—C, N—N, P—P and As—As linkages are 85.0, 48.0,

39.0 and 35.0 kcal/mol. Thus, the tendency of catenation decreases from N to P and from P to As. P and As can form a chain of only two atoms.

(i) Atomicity: Nitrogen is diatomic gaseous molecule at ordinary temperature. The existence of nitrogen as diatomic molecule is due to its ability to form multiple bonds. The molecule has one sigma and two  $\pi$ -bonds.

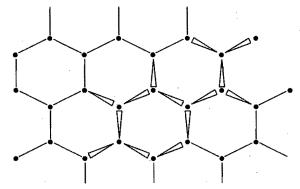
$$: N : N : or N : N = N : (N2)$$

The triple bond in nitrogen molecule is very stable as the dissociation energy is very high (225 kcal/mol). It is, therefore, inert under ordinary conditions.



**Fig. 10.1** X = P, As or Sb

Phosphorus, arsenic and antimony all exist as discrete tetratomic tetrahedral molecules, viz.,  $P_4$ ,  $As_4$  and  $Sb_4$  (Fig. 10.1) as these are not capable of forming multiple bonds due to repulsion between non-bonded electrons of the inner core. The angle between X-X-X is  $60^\circ$ . The  $p\pi-p\pi$  bonding in phosphorus, arsenic, etc., is therefore not possible. Elements of this group form giant lattice in which bonding changes from covalent to metallic, e.g., violet and red phosphorus has layer structure involving covalent bonding. Bismuth on the other hand involves purely metallic bonding. Metallic layer structure of bismuth is given below:



(j) Oxidation states: The elements of this group have five electrons in their outer shell. They exhibit a maximum oxidation state of +5 towards oxygen by using all the five electrons of outer shell. The tendency of the pair of ns electrons to remain inert (the inert pair effect) increases with increase of atomic number. Thus, only the p-electrons are used in bonding, i.e., +3 oxidation state is observed. +3 and +5 oxidation states

of these elements are observed with halogens and sulphur. The stability of +3 oxidation state increases and that of +5 oxidation state decreases on moving down from N to Bi.

Nitrogen and phosphorus generally exhibit -3 oxidation state due to high electronegativity and small size. Nitrogen forms nitride ion ( $N^{3-}$ ) with highly electropositive elements. Phosphorus also forms phosphide ion ( $P^{3-}$ ) to some extent. The tendency to show -3 oxidation state decreases from nitrogen to bismuth.

Note: Nitrogen besides -3, +3 and +5 oxidation states, exhibits a large number of oxidation states from -3 to +5; -3 in NH<sub>3</sub> and nitrides (Li<sub>3</sub>N, Ca<sub>3</sub>N<sub>2</sub>, AlN), -2 in NH<sub>2</sub>NH<sub>2</sub>, -1 in NH<sub>2</sub>OH, 0 in N<sub>2</sub>, +1 in N<sub>2</sub>O, +2 in NO, +3 in N<sub>2</sub>O<sub>3</sub> and HNO<sub>2</sub>, +4 in NO<sub>2</sub> and +5 in HNO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>.

**Disproportionation:** All the oxidation states of nitrogen from +1 to +4 show disproportionation in acidic medium. For example,

$$^{+3}_{3\text{HNO}_2} \xrightarrow{+5} ^{+2}_{100} + \text{H}_{20}$$

Phosphorus exhibits disproportionation in all the intermediate oxidation states from -3 to +5 in acidic and basic mediums. For example,

$$2H_{3}PO_{2} \xrightarrow{\text{Heat}} H_{3}PO_{4} + PH_{3}$$

$$+3 \xrightarrow{+5} -3$$

$$4H_{3}PO_{3} \longrightarrow 3H_{3}PO_{4} + PH_{3}$$

This tendency decreases from As to Bi due to inert pair effect as stability of +3 state increases from As to Bi.

(k) Valency and nature of bonding: There are five electrons present in the valence shell of these elements. To achieve stable configuration, they require three more electrons which is not easy to accept as to form trinegative ion  $(M^{3-})$ due to energy considerations. Such an ion is formed by nitrogen which is smallest and most electronegative element of the family when it combines with highly electropositive metals. This tendency is much less in phosphorus. These elements easily attain stable configuration by sharing three p-electrons, i.e., by forming three covalent bonds. Except nitrogen, all other elements have d-orbitals in the valence shell. As a result, one of the two ns-electrons may be promoted to nd-orbitals to have five unpaired orbitals in the valence shell. These can be used to form five covalent bonds. This is not possible in nitrogen as it has no d-orbitals (nitrogen never shows pentavalency). However, nitrogen can show a maximum covalency of 4 when it donates the *ns*-electron pair to Lewis acids.

Sb and Bi can lose three electrons forming  $M^{3+}$  ions but ionisation energy is too high for the other elements. Both SbF<sub>3</sub> and BiF<sub>3</sub>, exist as ionic solids. The  $M^{3+}$  ions are not very stable in solution. They can exist in fairly strong acid solution but are rapidly hydrolysed in water to give the antimony oxide ion or bismuth oxide ion, SbO<sup>+</sup> and BiO<sup>+</sup>. The change is reversed by adding 5M HCl.

$$Bi^{3+} \stackrel{H_2O}{\rightleftharpoons} [BiO]^+ + 2H^+$$

$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$$

$$Sb^{3+} + H_2O \rightleftharpoons [SbO]^+ + 2H^+$$
Antimonyl ion

**Multiple bonding:** Nitrogen forms  $p\pi - p\pi$  multiple bonds easily with itself and also with carbon and oxygen. Nitrogen exists as triply bonded diatomic gaseous molecule (N=N) at ordinary temperature. The bond strength is very high (941.4) kJ mol<sup>-1</sup>) and this is responsible for its inertness at ordinary conditions. Other members show reluctance to form multiple bonds. However, phosphorus can form  $p\pi$ - $d\pi$  type multiple bonds, e.g.,  $O = PX_3$ ,  $RN = PX_3$ .

Maximum covalency: The maximum covalency of nitrogen is four as it does not possess d-orbitals in the valence shell, i.e., it cannot extend its valency beyond four [NH<sub>4</sub>,  $R_4N^+$ ]. On the other hand, other members have empty d-orbitals and can utilise these orbitals to show covalency of five or six, e.g., PCl<sub>5</sub>, [SbF<sub>6</sub>].

(1) Thermal and electrical conductivity: Both these properties increase on moving down the group because delocalization of electrons increases from nitrogen to bismuth.

- 3. Occurrence: Nitrogen is found in free as well as in combined state. Nitrogen forms 75% by mass and 78% by volume of the atmosphere. In the combined state, it occurs as nitrates, proteins, amino acids, etc. Phosphorus does not occur free in nature. Phosphorus is the eleventh most abundant element in the earth's crust. Phosphorus is essential for life of both plants and animals. About 60% of bones and teeth are Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> or [3{Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>}.CaF<sub>2</sub>] and an average person has 3.5 kg of calcium phosphate in his body. Phosphorus is present, in DNA, RNA, ATP, ADP, etc. It is also found as phosphates in nature. As, Sb and Bi are not abundant. They occur as sulphides or oxides.
- 4. Chemical properties: Elements of this group differ from one another appreciably in their chemical activity. Nitrogen is chemically inert under ordinary conditions. Due to this reason, it is found free in atmosphere. The chemical inertness is due to high stability of the triple bond between the two nitrogen atoms. The dissociation energy of the bond is high, i.e., 225 kcal per mole. It is, therefore, at high temperature only when nitrogen can react with other elements.

Phosphorus especially white form is extremely reactive. It readily burns in oxygen to form oxides. The strained structure of P<sub>4</sub> is responsible for high chemical activity. The heavier elements are less reactive as they burn only when heated in air or oxygen to form oxides.

(a) Oxides: All these elements form oxides of the type  $X_2O_3$ ,  $X_2O_4$  and  $X_2O_5$ .

Element Nitrogen Phosphorus Arsenic Antimony Bismuth

Type of oxides				,	. 1
$X_2O_3$	$N_2O_3$	$P_2O_3$	$As_2O_3$	$Sb_2O_3$	Bi <sub>2</sub> O <sub>3</sub>
$X_2O_4$	$N_2O_4$	$P_2O_4$	$As_2O_4$	$Sb_2O_4$	Bi <sub>2</sub> O <sub>4</sub>
$X_2O_5$	$N_2O_5$	$P_2O_5$	$As_2O_5$	$Sb_2O_5$	Bi <sub>2</sub> O <sub>5</sub>

Acidic nature decreases

Greater is the electronegativity more is the acidic character of its oxide. Moreover, among the oxides of same element higher oxidation state is responsible for greater acidic character.

Besides these three types of oxides, nitrogen forms two more oxides N<sub>2</sub>O and NO (these are neutral) and bismuth forms bismuth monoxide (BiO).

#### (i) Acidic nature of each type decreases from nitrogen to bismuth.

N<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>3</sub> are acidic, As<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub> are amphoteric while Bi<sub>2</sub>O<sub>3</sub> is more basic and less acidic.

$$\begin{array}{c} N_2O_3 + H_2O \longrightarrow 2HNO_2 \text{ (Nitrous acid)} \rightarrow \text{acidic} \\ P_2O_3 + 3H_2O \longrightarrow 2H_3PO_3 \text{ (Phosphorus acid)} \rightarrow \text{acidic} \\ As_2O_3 + 6HCl \longrightarrow 2AsCl_3 + 3H_2O \longrightarrow \text{basic} \\ As_2O_3 + 6NaOH \longrightarrow 2Na_3AsO_3 + 3H_2O \rightarrow \text{acidic} \\ Sb_2O_3 + 6HCl \longrightarrow 2SbCl_3 + 3H_2O \longrightarrow \text{basic} \\ Sb_2O_3 + 6NaOH \longrightarrow 2Na_3SbO_3 + 3H_2O \longrightarrow \text{acidic} \\ Sb_2O_3 + 6NaOH \longrightarrow 2Na_3SbO_3 + 3H_2O \longrightarrow \text{acidic} \\ Bi_2O_3 + 6HCl \longrightarrow 2BiCl_3 + 3H_2O \longrightarrow \text{basic} \\ \end{array}$$

Bi<sub>2</sub>O<sub>3</sub> shows feeble acidic character also as it slightly dissolves in concentrated NaOH solution.

$$Bi_2O_3 + 6NaOH \longrightarrow 2Na_3BiO_3 + 3H_2O$$
Sodium bismuthite

The acidic nature of pentoxides decreases from N<sub>2</sub>O<sub>5</sub> to Bi<sub>2</sub>O<sub>5</sub>·N<sub>2</sub>O<sub>5</sub>, P<sub>2</sub>O<sub>5</sub> and As<sub>2</sub>O<sub>5</sub> are soluble in water and form acids.

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$
 (Nitric acid)  
 $P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$  (Orthophosphoric acid)  
 $As_2O_5 + 3H_2O \longrightarrow 2H_3AsO_4$  (Arsenic acid)

Sb<sub>2</sub>O<sub>5</sub> and Bi<sub>2</sub>O<sub>5</sub> are insoluble in water but dissolve in

Acidic nature of  $M_2O_4$  oxides also decreases from  $N_2O_4$  to  $Bi_2O_4$ . The acidic nature of these oxides is less than  $X_2O_5$  type and more than  $X_2O_3$  type. The decrease in acidic nature of the oxides from nitrogen to bismuth is due to decrease in nonmetallic character and increase in metallic character from N to Bi.

(ii) In the oxides of a particular element, the acidic nature increases as the percentage of oxygen increases or as the oxidation state increases. For example, N2O5 is most acidic while N<sub>2</sub>O<sub>3</sub> is less acidic, similarly P<sub>2</sub>O<sub>5</sub> is more acidic than  $P_2O_3$  and  $P_2O_4$ .

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$
  
 $N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$   
 $N_2O_5 + H_2O \longrightarrow 2HNO_3$ 

HNO<sub>3</sub> is stronger than HNO<sub>2</sub>.

$$P_2O_3 + 3H_2O \longrightarrow 2H_3PO_3$$
  
 $P_2O_4 + 3H_2O \longrightarrow H_3PO_4 + H_3PO_3$   
 $P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$ 

H<sub>3</sub>PO<sub>4</sub> is stronger than H<sub>3</sub>PO<sub>3</sub>.

(iii) Stability of oxides of higher oxidation states decreases with increasing atomic number.

Thermal stability decreases in each series from N to Bi  $N_2O_3$  is most stable oxide. It is more stable than other oxides.  $N_2O_5$  is less stable. However,  $P_2O_5$  is thermally stable, but  $As_2O_5$  and  $Sb_2O_5$  are less stable.  $Bi_2O_5$  is least stable. Except  $P_2O_5$ , all the pentoxides show oxidising properties.  $N_2O_5$  is the strongest oxidising agent.

Nitrogen forms two more oxides, nitrous oxide ( $N_2O$ ) and nitric oxide (NO). Both are neutral in nature. Structurally, the oxides of nitrogen are different from the oxides of the rest of the elements of this group. This is due to the fact that only nitrogen is able to form  $p\pi$ - $p\pi$  multiple bonds which are present in its oxides. The rest of the elements do not form multiple bonds and prefer to form cage structures for their oxides.

(b) Oxyacids: All the elements of this group form oxyacids. Nitrogen forms a number of oxyacids but two common oxyacids are—nitrous acid (HNO<sub>2</sub>) and nitric acid (HNO<sub>3</sub>). Nitric acid is a stable acid while HNO<sub>2</sub> is unstable. Phosphorus forms a large number of oxyacids. The important oxyacids are:

$H_3PO_2$	$H_3PO_3$	$H_4P_2O_4$
Hypophosphorus	Phosphorus	Hypophosphoric
acid	acid	acid
$H_3PO_4$	$HPO_3$	$H_4P_2O_7$
Orthophosphoric	Metaphosphoric	Pyrophosphoric .
acid	acid	acid

Arsenic forms two oxyacids, H<sub>3</sub>AsO<sub>3</sub> (arsenious acid) and H<sub>3</sub>AsO<sub>4</sub> (arsenic acid). Antimony forms one oxyacid H<sub>3</sub>SbO<sub>3</sub> which exists in solution. Bismuth also forms one stable oxyacid HBiO<sub>3</sub>, meta-bismuthic acid.

The strength and stability of oxyacids having the element in the same oxidation state decreases gradually with decrease in electronegativity of central atom.

(c) **Hydrides:** All the elements of this group form hydrides of the type  $MH_3$ .

(i) All the hydrides are formed by the action of water or dilute acids on binary metallic compounds such as Mg<sub>3</sub>N<sub>2</sub>, Ca<sub>3</sub>P<sub>2</sub>, Zn<sub>3</sub>As<sub>2</sub>, Mg<sub>3</sub>Sb<sub>2</sub> and Mg<sub>3</sub>Bi<sub>2</sub>.

The hydrides are also obtained by reduction of trichlorides of these elements (except that of bismuth) with Zn/acid or LiAlH<sub>4</sub>.

$$4MCl_3 + 3LiAlH_4 \longrightarrow 4MH_3 + 3LiCl + 3AlCl_3$$
  
( $M = N, P, As, Sb$ )

- (ii) All the hydrides are colourless gases. Their smell becomes more and more disagreeable as atomic number increases from N to Bi.
  - (iii) The poisonous nature increases from NH<sub>3</sub> to BiH<sub>3</sub>.
- (iv) NH<sub>3</sub> is highly soluble in water but other hydrides are less soluble.
- (v) The basic character decreases from NH<sub>3</sub> to BiH<sub>3</sub>. The basic nature is due to the presence of lone pair of electrons on the central atom. NH<sub>3</sub> is the strongest electron pair donor due to its small size as the electron density of the electron pair is concentrated over a small region. As the size increases the electron density gets diffused over a large region and hence the ability to donate the electron pair (basic nature) decreases. NH<sub>3</sub> and PH<sub>3</sub> form NH<sub>4</sub><sup>+</sup> and PH<sub>4</sub><sup>+</sup> ions with protons. NH<sub>4</sub><sup>+</sup> is more stable than PH<sub>4</sub><sup>+</sup> ion. PH<sub>3</sub> is less basic than NH<sub>3</sub> while AsH<sub>3</sub>, SbH<sub>3</sub> and BiH<sub>3</sub> are neutral. NH<sub>3</sub> is highly soluble in water while PH<sub>3</sub> is less soluble.

(vi) Thermal stability decreases gradually from NH<sub>3</sub> to BiH<sub>3</sub>. The decomposition temperatures decrease from NH<sub>3</sub> to BiH<sub>3</sub>.

The size of the central atom increases from N to Bi, therefore, the tendency to form a stable covalent bond with small hydrogen atom decreases. As the bond length increases, the strength decreases and therefore, thermal stability decreases.

(vii) The reducing nature increases. This shows that bond strength M—H decreases as electronegativity of M decreases.

NH<sub>3</sub> is a weak reducing agent while AsH<sub>3</sub>, SbH<sub>3</sub> and BiH<sub>3</sub> are powerful reducing agents.

(viii) The shape of these hydrides is pyramidal. The formation is due to  $sp^3$  hybridization of central atom, *i.e.*, forming a tetrahedral configuration. However, on one of tetrahedral positions, a lone pair of electrons is present. The bond angle (HMH) in various hydrides is never equal to ideal tetrahedral angle of 109°28′. The actual bond angles are:

The bond angle in ammonia is less than  $109^{\circ}28'$  due to repulsion between lone pair present on nitrogen atom and bonded pairs of electrons. The decreased bond angle in other hydrides can be explained by the fact that the  $sp^3$  hybridization becomes less and less distinct with increasing size of the central atom, *i.e.*, pure p-orbitals are utilised in M—H bonding.

Bond lengths and bond dissociation energies of the hydrides of group 15 elements are listed below:

Hydride	NH <sub>3</sub>	$PH_3$	AsH <sub>3</sub>	SbH <sub>3</sub>
M-H bond length (pm)	101.7	141.9	151.9	170.7
M-H dissociation energy	391	322	297	255
(kJ mol <sup>-1</sup> )				

- (ix) **Hydrogen bonding:** Hydrogen bonding is present in NH<sub>3</sub> as the electronegativity difference between nitrogen and hydrogen is high and the N—H bond shows polarity. The electronegativity of rest of the elements is nearly equal to hydrogen, hence *M*—H bond is purely covalent and no hydrogen bonding is present in their hydrides.
  - (x) The boiling points of these hydrides vary as follows:

Hydride	$NH_3$	$PH_3$	$AsH_3$	$SbH_3$	$BiH_3$
Boiling point (°C)	-33	-89	-63	<del>9</del>	17

In NH<sub>3</sub>, molecules are associated by hydrogen bonding and thus its boiling is comparatively high in comparison to PH<sub>3</sub> and AsH<sub>3</sub> where no hydrogen bonding is present. In moving from PH<sub>3</sub> to BiH<sub>3</sub>, boiling points increase due to increase in the magnitude of van der Waals' forces due to increase in molecular size.

(d) Halides: The main halides formed by the elements of this group are listed below:

Element	Trihalides	Pentahalides
Nitrogen	NF <sub>3</sub> , NCl <sub>3</sub> , NBr <sub>3</sub> , NI <sub>3</sub>	· · • <u>• · ·</u> • · · • ·
Phosphorus	PF <sub>3</sub> , PCl <sub>3</sub> , PBr <sub>3</sub> , PI <sub>3</sub>	PCl <sub>5</sub> , PF <sub>5</sub> , PBr <sub>5</sub>
Arsenic .	AsF <sub>3</sub> , AsCl <sub>3</sub> , AsBr <sub>3</sub> , AsI <sub>3</sub>	AsF <sub>5</sub>
Antimony	SbF <sub>3</sub> , SbCl <sub>3</sub> , SbBr <sub>3</sub> , SbI <sub>3</sub>	SbF <sub>5</sub> , SbCl <sub>5</sub>
Bismuth	BiF <sub>3</sub> , BiCl <sub>3</sub> , BiBr <sub>3</sub> , BiI <sub>3</sub>	$\mathrm{BiF}_{5}$

All form trihalides. One or more pentahalides are formed by the elements except nitrogen. Nitrogen does not form pentahalides due to absence of *d*-orbitals.

(i) **Trihalides:** The elements directly combine with halogens and form trihalides,  $MX_3$ . All the trihalides are stable except NCl<sub>3</sub>, NBr<sub>3</sub> and NI<sub>3</sub>. The unstable nature of NCl<sub>3</sub>, NBr<sub>3</sub> and NI<sub>3</sub> is due to low polarity of N—X bond and a large difference in the size of nitrogen and halogen atoms.

The trihalides have a tetrahedral structure involving  $sp^3$ -hybridization of the central atom. They have pyramidal shape. A lone pair of electrons is present on the central atom. Due to the presence of a lone pair of electrons on the central atom, they act as Lewis bases. In the case of nitrogen halides, the tendency to act as Lewis base decreases from NI<sub>3</sub> to NF<sub>3</sub>.

$$NI_3 > NBr_3 > NCl_3 > NF_3$$

This is due to increased electronegativity from I to F.

Also the tendency to act as Lewis base decreases from N to Bi for a given halide.

The trihalides of phosphorus and antimony especially fluorides and chlorides act as Lewis acids also by using the vacant *d*-orbitals.

Except NF<sub>3</sub> and PF<sub>3</sub>, all the trihalides are hydrolysed by water.

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HClO$$
  
 $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$   
 $AsCl_3 + 3H_2O \longrightarrow H_3AsO_3 + 3HCl$   
 $SbCl_3 + H_2O \Longrightarrow SbOCl + 2HCl$   
 $BiCl_3 + H_2O \Longrightarrow BiOCl + 2HCl$ 

**Note:** The NCl<sub>3</sub> is hydrolysed to a base (NH<sub>3</sub>) while PCl<sub>3</sub> is hydrolysed to an acid (H<sub>3</sub>PO<sub>3</sub>). It is due to the fact that NCl<sub>3</sub> is an electron pair donor while PCl<sub>3</sub> is an acceptor as P has vacant 3*d*-orbitals.

(ii) **Pentahalides:** Phosphorus pentachloride is the most well known of the pentahalides. Bismuth does not form pentahalides because of inert pair effect. The pentahalides have a trigonal bipyramid shape  $(sp^3d$ -hybridization) in gaseous and liquid states which is not very stable structure, hence these pentahalides decompose into stable lower halides.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

These are also hydrolysed by water.

$$PCl_5$$
 +  $H_2O \longrightarrow POCl_3 + 2HCl$   
 $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$ 

[PCl<sub>5</sub> acts as an effective chlorinating agent.]

X-ray studies have shown that the solid PCl<sub>5</sub> is an ionic compound composed of [PCl<sub>4</sub>]<sup>+</sup> [PCl<sub>6</sub>]<sup>-</sup>. Solid PBr<sub>5</sub> exists as [PBr<sub>4</sub>]<sup>+</sup>Br<sup>-</sup>.

All the pentahalides act as Lewis acids due to the presence of d-orbitals.

$$MX_5 + X^- \longrightarrow [MX_6]^-$$

The hybridization of the central atom (M) changes from  $sp^3d$  to  $sp^3d^2$ .

(e) Sulphides: With the exception of nitrogen, all other elements of this group form sulphides. The sulphides of arsenic and antimony are soluble in yellow ammonium sulphide or ammonium sulphide and form thio-compounds.

Antimony sulphides form similar compounds. The sulphides are also soluble in caustic alkali.

$$As_2S_3 + 6NaOH \longrightarrow Na_3AsS_3 + Na_3AsO_3 + 3H_2O$$
Sodium thio-
arsenite

Sodium
arsenite

The stability of sulphides increases with increase in atomic number of the element.

# 10.22 ABNORMAL BEHAVIOUR OF NITROGEN

Nitrogen differs considerably from the rest of the family members. The differences or abnormal properties are mainly due to the following four factors:

- (a) Small size of nitrogen atom.
- (b) High value of electronegativity.
- (c) Absence of d-orbitals in the valency shell.
- (d) Tendency to form multiple bonds.

The important points in which nitrogen differs from other members of VA group are listed below:

- (i) Nitrogen is a gas while other members are solids.
- (ii) Nitrogen molecule is diatomic (N≡N) while other elements form tetratomic molecules such as P<sub>4</sub>, As<sub>4</sub> and Sb<sub>4</sub>.
- (iii) The catenation property is more pronounced in nitrogen. Chains containing upto eight nitrogen atoms are known but in the case of other elements, catenation is limited to two atoms only.
- (iv) Nitrogen forms five oxides.  $N_2O$  (nitrous oxide), NO (nitric oxide),  $N_2O_3$  (nitrogen trioxide),  $NO_2$  (nitrogen dioxide) and  $N_2O_5$  (nitrogen pentoxide). Others can form at the most three types of oxides,  $X_2O_3$ ,  $X_2O_4$  and  $X_2O_5$ .

 $N_2O_3$  and  $N_2O_5$  are monomeric in nature but oxides of other elements are dimeric.

- (v) Hydride of nitrogen (NH<sub>3</sub>) is stable while the hydrides of other elements are not stable. Hydrogen bonding is present in ammonia (NH<sub>3</sub>) but not present in other hydrides.
- (vi) Except  $NF_3$ , the halides of nitrogen ( $NCl_3$ ,  $NBr_3$  and  $NI_3$ ) are unstable and explosive. The halides of other elements are stable. Unlike P, As and Sb, nitrogen does not form pentahalides.
- (vii) Due to small size and high electronegativity, nitrogen can form trinegative ion  $N^{3-}$ . This tendency is less in P but absent in other elements.
- (viii) As nitrogen does not have *d*-orbitals in its valency shell, its maximum covalency is 3 while in the case of other elements, the maximum covalency is 5.
- (ix) Nitrogen is chemically inert under ordinary atmospheric conditions. This is due to high dissociation energy of nitrogen molecule. The other elements are quite reactive as they have single bonds in their molecules, *i.e.*, dissociation energies are low.
- (x) Nitrogen shows a large number of oxidation states from -3 to +5 such as +1 in  $N_2O_5$ , +2 in  $NO_5$ , +3 in  $N_2O_3$ , +4 in  $NO_2$ , +5 in  $N_2O_5$ , -1 in  $NH_2OH$  and -3 in  $NH_3$ . Other elements show a limited number of oxidation states from -3 to +5.
- (xi) Nitrogen does not form sulphide while all other elements form sulphides.
- (xii) On account of high value of electronegativity, nitrogen behaves as a typical non-metal while As, Sb are metalloids and Bi is a metal.

Nitrogen (N≡N), carbon monoxide C ∓O and cyanide ion (C≡N) are isoelectronic in nature. Nitrogen is inert while other species are active. The bond between nitrogen atoms is non-polar.

#### 10.3 NITROGEN (N<sub>2</sub>)

Scheele, in 1772, showed that air is a mixture of two gases: fire air (oxygen) which supports combustion and respiration and foul air (nitrogen) which does not take part in combustion. D. Rutherford named foul air as mephitic air (killer of life). Later on the element was found to be present in nitre and thus, the name **nitrogen** was proposed.

Occurrence: Nitrogen exists in its elemental form as diatomic molecules (N<sub>2</sub>), it is therefore, called as dinitrogen. Nitrogen is widely distributed in nature both in free as well as in the combined state. Air is the most abundant source of free nitrogen. It forms 75% by mass and 78% by volume of the air. In combined state, it is found as nitrates such as Chile saltpetre (NaNO<sub>3</sub>), Indian saltpetre (KNO<sub>3</sub>) and ammonium compounds. It is an essential constituent of all living things (animals and vegetables both) where it is found in the form of proteins, amino acids and nucleic acids. Its existence in atmosphere is very important because it acts as inert diluent for the highly reactive gas, *i.e.*, oxygen. Without nitrogen, every spark in our atmosphere would cause a massive fire.

**Preparation:** Nitrogen can be obtained from the following two sources:

- (i) Nitrogen compounds and (ii) Air.
- (i) From nitrogen compounds: (a) Nitrogen in the laboratory can be obtained by heating ammonium nitrite or ammonium dichromate. Ammonium nitrite is not a stable compound and thus it is first formed as an intermediate product by heating an ammonium salt with sodium nitrite.

$$\begin{array}{c} NH_4Cl + NaNO_2 \longrightarrow NH_4NO_2 + NaCl \\ \\ NH_4NO_2 \longrightarrow N_2 + 2H_2O \\ \\ (NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O \end{array}$$

Nitrogen is collected by downward displacement of water.

(b) Pure nitrogen can be obtained by passing the ammonia vapours over heated CuO.

$$2NH_3 + 3CuO \longrightarrow N_2 + 3Cu + 3H_2O$$

NH<sub>3</sub> can also be oxidised to nitrogen by Cl<sub>2</sub>, Br<sub>2</sub>, a hypochlorite, a hypobromite or bleaching powder. [See for reactions section 10.4.]

(c) It can also be obtained by the action of nitrous acid (or NaNO<sub>2</sub> and dil. H<sub>2</sub>SO<sub>4</sub>) on urea.

$$NH_2CONH_2 + 2HNO_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$$
Urea

(d) Pure nitrogen is obtained in small amount by heating sodium or barium azides in vacuum.

$$Ba(N_3)_2 \longrightarrow 3N_2 + Ba$$

(ii) From air: (a) Air is the major source of nitrogen. Commercially nitrogen is obtained by liquefaction of air. The resultant liquid is fractionally distilled in *Claude's apparatus*.

Air is freed from dust particles and compressed to 60 atmospheres. It is cooled. The compressed air is freed from CO<sub>2</sub> by passing through a tower packed with sodalime and then dried by passing through alumina driers. It is then passed through pipes which are surrounded by cold nitrogen or cold oxygen. The cold compressed air is allowed to do work in Claude's expansion engine when it is partially liquefied. The partially liquefied air is passed through a double rectification column when more of air is liquefied. Liquefied air is further fractionally distilled in Claude's apparatus. Finally, about 90% pure nitrogen escapes through the exit at the top of the apparatus.

(b) By removing oxygen of the air with the use of chemical substances.

Purified air 
$$\longrightarrow$$
 Hot Cu  $\longrightarrow$  Nitrogen  $2\text{Cu} + \text{O}_2 \longrightarrow 2\text{CuO}$  Purified air  $\longrightarrow$  Hot coke  $\longrightarrow$  CO<sub>2</sub>, CO, N<sub>2</sub> CO<sub>2</sub> and CO are removed by usual methods. Purified air  $\longrightarrow$  Phosphorus  $\longrightarrow$  P<sub>2</sub>O<sub>5</sub> + N<sub>2</sub>  $\longrightarrow$  H<sub>2</sub>O

**Properties:** (i) It is a colourless, tasteless and odourless gas. It is slightly lighter than air as its vapour density is 14.0. It is sparingly soluble in water.

- (ii) It is not poisonous in nature but animals do not survive in its atmosphere due to absence of oxygen.
- (iii) It can be liquefied to a colourless liquid (b.pt. -195.8°C). When liquid nitrogen is poured on a table, the liquid sizzles and boils away violently.
- (iv) It does not help in combustion. Nitrogen itself is non-combustible.
- (v) It is chemically inert under ordinary conditions. However, it shows chemical activity under high temperatures.
- (a) Nitrogen combines with oxygen under the influence of very high temperature like electric spark.

$$N_2 + O_2 \stackrel{3000^{\circ}C}{\rightleftharpoons} 2NO \text{ (Nitric oxide)}$$

(b) Nitrogen combines with hydrogen in the presence of a catalyst (finely divided iron) at 200 atmospheres and 400–500°C temperature.

$$N_2 + 3H_2 \Longrightarrow 2NH_3$$
 (Ammonia)

(c) Nitrogen combines with metals at red heat to form nitrides.

$$\begin{array}{l} 6\text{Li} + \text{N}_2 \xrightarrow{\phantom{0}450^{\circ}\text{C}} 2\text{Li}_3\text{N (Lithium nitride)} \\ 3\text{Mg} + \text{N}_2 \xrightarrow{\phantom{0}450^{\circ}\text{C}} \text{Mg}_3\text{N}_2 \text{ (Magnesium nitride)} \\ 2\text{Al} + \text{N}_2 \xrightarrow{\phantom{0}800^{\circ}\text{C}} 2\text{AlN (Aluminium nitride)} \end{array}$$

Non-metals like boron, silicon at bright red heat also combine with nitrogen.

$$2B + N_2 \longrightarrow 2BN$$
 (Boron nitride)  
 $3Si + 2N_2 \longrightarrow Si_3N_4$  (Silicon nitride)

(d) Nitrogen combines with calcium carbide to form calcium cyanamide at 1000°C.

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

The mixture of calcium cyanamide and carbon is technically known as nitrolim.

(e) When nitrogen is passed over heated mixture of alumina and carbon, aluminium nitride is formed.

$$Al_2O_3 + 3C + N_2 \xrightarrow{1273 \text{ K}} 2AlN + 3CO$$

This reaction is used for the purification of alumina ore (Serpeck's process). AlN is hydrolysed with steam.

$$\begin{array}{c} AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3 \\ & \downarrow \text{Heated} \\ & Al_2O_3 \\ \text{Pure alumina} \end{array}$$

- **Uses:** (i) Nitrogen,  $N_2$ , is a relatively unreactive element because of the stability of the nitrogen-nitrogen triple bond (The N = N bond energy is 942 kJ/mol compared with 167 kJ/mol for the N N bond energy). Therefore, it is used to provide an inert atmosphere in certain metallurgical operations and during welding.
- (ii) Large quantity of nitrogen is used as a blanketing gas, the purpose of which is, to protect a material from oxygen during processing or storage. Thus, electronic components are often made under a nitrogen atmosphere.
  - (iii) It is used for filling electric bulbs.
- (iv) It is used in the manufacture of NH<sub>3</sub>, HNO<sub>3</sub>, CaCN<sub>2</sub> and other nitrogen compounds.
- (v) Liquid nitrogen is used as a refrigerant to freeze foods, to freeze soft or rubbery materials prior to grinding them, and to freeze biological materials. Liquid nitrogen has found wide use in frozen food preparation and preservation during transit.
- (vi) Liquid nitrogen is also a cryogen. It has uses in medicine (cryosurgery), for example in cooling a localized area of skin prior to removal of a wart or other unwanted or pathogenic tissue.

#### Active Nitrogen

When an electric discharge is allowed to pass through nitrogen under very low pressure (about 2 mm), a brilliant luminiscence is observed which persists for sometime after the stoppage of the discharge. It is observed that nitrogen after the discharge is more active. This nitrogen is termed active nitrogen.

This form is not quite stable and gradually changes to normal form. Active nitrogen reacts readily with many metals to form

nitrides. It reacts with a number of non-metals, e.g., sulphur, phosphorus, iodine, etc. It is able to decompose many organic compounds.

$$C_2H_2 + N_2 \longrightarrow C_2N_2 + H_2$$
Active

The exact nature of active nitrogen is not yet known.

#### 10.4 IMPORTANT COMPOUNDS OF NITROGEN

#### 🕾 1. Ammonia

Nitrogen forms three well known hydrides with hydrogen: (i) Ammonia, NH<sub>3</sub>, (ii) Hydrazine, NH<sub>2</sub>.NH<sub>2</sub> (N<sub>2</sub>H<sub>4</sub>), (iii) Hydrazoic acid, N<sub>3</sub>H. Ammonia is the most important of these hydrides.

**Occurrence:**  $_{\mathbf{\ell}}$  NH<sub>3</sub> is found in traces in atmosphere. This is formed by bacterial decomposition of nitrogenous matter of plants and animals. Ammonium salts such as ammonium chloride and ammonium sulphate are found in small amounts in the soil. On certain planets (Jupiter and Saturn), it is found in abundance.

**Discovery:** It was first isolated in 1774 by Priestley by the action of ammonium chloride and lime. It was named alkaline air. Berthelot, in 1788, pointed out that ammonia is a compound of nitrogen and hydrogen. In 1800, Davy established its formula NH<sub>3</sub>.

**Preparation:** (i) Ammonia is obtained on a small scale from ammonium salts which evolve it when heated with caustic soda or lime.

$$NH_4Cl + NaOH \longrightarrow NH_3 + NaCl + H_2O$$
  
 $2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$   
(Slaked lime)

(ii) Ammonia is formed when ammonium chloride is heated with litharge.

$$2NH_4Cl + PbO \longrightarrow 2NH_3 + PbCl_2 + H_2O$$

(iii) By reacting nitrides with water, ammonia is obtained.

$$\begin{aligned} \text{AlN} + 3\text{H}_2\text{O} &\longrightarrow \text{Al}(\text{OH})_3 + \text{NH}_3 \\ \text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} &\longrightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3 \end{aligned}$$

(iv) Ammonia can also be formed by doing reduction of nitrates and nitrites with zinc and caustic soda. Zinc and caustic soda produce nascent hydrogen which reacts with nitrates and nitrites to form ammonia.

$$NaNO_3 + 8H \xrightarrow{Zn/NaOH} NaOH + NH_3 + 2H_2O$$

$$NaNO_2 + 6H \xrightarrow{Zn/NaOH} NaOH + NH_3 + H_2O$$

(v) Calcium cyanamide on hydrolysis evolves ammonia.CaCN<sub>2</sub> + 3H<sub>2</sub>O → CaCO<sub>3</sub> + 2NH<sub>3</sub>

(vi) Ammonia is also obtained by heating ammonium compounds.

$$\begin{array}{ccc} (NH_4)_2SO_4 & \xrightarrow{Heat} NH_3 + & NH_4HSO_4 \\ \text{Ammonium} & & & \text{Ammonium hydrogen} \\ \text{sulphate} & & & \text{sulphate} \end{array}$$

(vii) Urea on treatment with caustic soda forms ammonia.

$$NH_2CONH_2 + 2NaOH \longrightarrow Na_2CO_3 + 2NH_3$$
Urea

**Laboratory preparation:** Ammonia is prepared in the laboratory by heating ammonium chloride with slaked lime,  $Ca(OH)_2$  in the ratio of 3:2 in apparatus shown in Fig. 10.2.

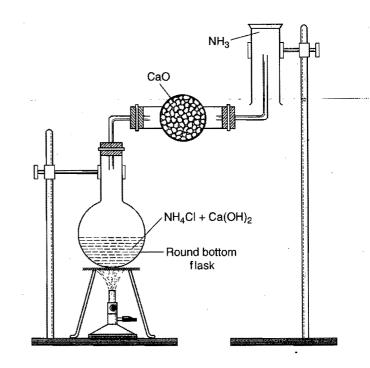


Fig. 10.2 Apparatus for laboratory preparation of ammonia

The mixture is taken in a flask and heated gently. The gas evolved is passed through lime tube and finally collected in a dry jar by downward displacement of air method.

**Precautions:** (i) The apparatus should be air tight.

- (ii) For the collection of gas, dry cylinders should be used as it is very soluble in water.
- (iii) The contents in a flask be covered with a layer of calcium hydroxide as to absorb water otherwise the flask will crack.
- (iv) For drying of ammonia gas, the common dehydrating agents like sulphuric acid or CaCl<sub>2</sub> or P<sub>2</sub>O<sub>5</sub> cannot be used as these react with ammonia.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$
Ammonium sulphate
$$CaCl_2 + 8NH_3 \longrightarrow CaCl_2 \cdot 8NH_3$$
Addition product
$$P_2O_5 + 6NH_3 + 3H_2O \longrightarrow 2(NH_4)_3PO_4$$
Ammonium phosphate

For drying, quick lime, CaO is used as it does not react with ammonia but reacts readily with moisture.

$$\begin{array}{ccc} \text{CaO} & + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 \\ \text{Quick lime} \end{array}$$

#### Manufacture of Ammonia

#### (i) Haber process:

**Principle:** Haber process is the most important industrial method of preparing ammonia from  $N_2$  and  $H_2$ . This method was discovered by a German chemist **Fritz Haber** in 1913. He was awarded Nobel Prize in 1918 for this work. The method involves the direct combination of nitrogen and hydrogen according to the following reaction:

$$N_2 + 3H_2 \Longrightarrow 2NH_3 + 24.0 \text{ kcal}$$

The reaction is reversible, exothermic and formation of NH<sub>3</sub> is followed by a decrease in volume. According to Le Chatelier's principle, the optimum conditions for the greater yield of ammonia are:

- (a) **High pressure:** Usually a pressure of 200 atmospheres is applied.
- **(b) Low temperature:** The working temperature of 450-550°C is maintained, since reaction is very slow below this temperature.
- **(c) Catalyst:** At low temperature, although the yield of ammonia is more yet the reaction is very slow. In order to speed up the reaction, a catalyst is used. The following catalysts have been proposed for this purpose:
  - (i) Finely divided iron with some molybdenum as a promoter.
- (ii) Finely divided nickel and sodalime deposited over pumice stone.
  - (iii) Finely divided osmium or uranium.

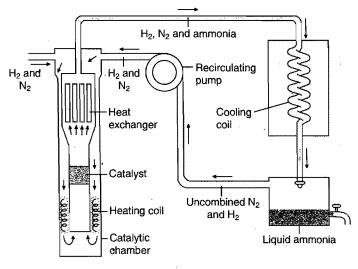
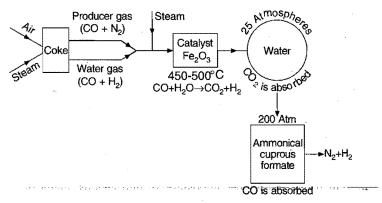


Fig. 10.3

Impure gases poison the catalyst; hydrogen and nitrogen used, therefore, be free from CO, etc., which can spoil the working of the catalyst.

Raw materials: Nitrogen and hydrogen are the chief raw materials. Nitrogen is obtained from air by liquefaction followed by fractional evaporation of liquid air. Hydrogen is obtained by electrolysis of water.

The gaseous mixture containing nitrogen and hydrogen is thoroughly dried before it is used for the formation of ammonia.



**Method:** The mixture of nitrogen and hydrogen in the ratio of 1:3 is compressed to 200 atmospheric pressure and allowed to enter the ammonia converter [Fig. 10.4 (a)] at the base.

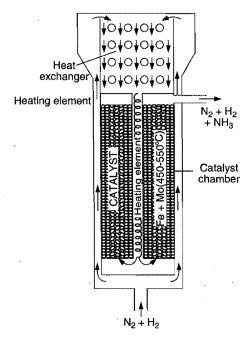


Fig. 10.4 (a) Ammonia converter

The gases are heated to 450-500°C. The gases now enter the catalyst chamber and interact forming ammonia. The issuing gases containing about 10% ammonia are cooled in water cooler when some ammonia liquefies. The remaining ammonia is removed from gaseous mixture by dissolving in water. The unreacted N<sub>2</sub> and H<sub>2</sub> are mixed with fresh gases and recirculated through the converter. A diagrammatic sketch of the plant is shown in Fig. 10.4 (b).

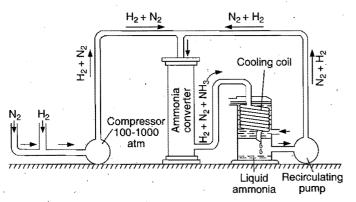


Fig. 10.4 (b)

 $CO_2$  absorbed in the water during the manufacture of  $N_2$  and  $H_2$  by Haber-Bosch process can be utilised for the manufacture of urea or ammonium sulphate from gypsum.

$$2NH_3 + CO_2 \xrightarrow{100\text{-}300 \quad atm.} NH_2COONH_4 \rightarrow NH_2CONH_2 + H_2O$$

$$\xrightarrow{Ammonium} \qquad Urea$$

$$carbamate$$

$$CaSO_4 + 2NH_4OH + CO_2 \longrightarrow (NH_4)_2SO_4 + CaCO_3 + H_2O$$

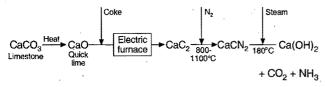
$$\xrightarrow{Ammonium} \qquad sulphate$$

#### (ii) Cyanamide process:

The calcium cyanamide is formed by the action of nitrogen on calcium carbide at 800-1100°C. It is then treated with superheated steam at 180°C under a pressure of 3 to 4 atmospheres when ammonia is produced.

$$CaCN_2 + 4H_2O \longrightarrow Ca(OH)_2 + CO_2 + 2NH_3$$

The flow sheet for this industry is given below:



Now-a-days low temperature (500-600°C) is used under 6-8 atmospheric pressure.

#### Physical properties:

- (i) Ammonia, NH<sub>3</sub>, is the most important commercial compound of nitrogen. It is a colourless gas with a characteristic irritating or pungent odour. It brings tears into the eyes.
  - (ii) It is lighter than air.
- (iii) It is highly soluble in water. One volume of water dissolves 1300 volumes of ammonia at 0°C and 1 atmosphere. The high solubility is due to the hydrogen bonding. The solubility of ammonia increases with increase of pressure and decreases with increase of temperature.

- (iv) It can be easily liquefied at room temperature by the application of pressure. The liquid ammonia is colourless and boils at -33°C. It freezes at -78°C. Liquid ammonia has a large heat of vaporisation (327 cal/g). It is, therefore, used in iceplants.
- (v) Ammonia molecules link together to form associated molecules through hydrogen bonding.

Higher melting point and boiling point in comparison to other hydrides of V group are due to hydrogen bonding.

#### Chemical properties:

(i) Stability: It is highly stable. It decomposes into nitrogen and hydrogen at red heat or when electric sparks are passed through it.

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

(ii) Combustion: Ordinary, ammonia is neither combustible nor a supporter of combustion. However, it burns in the presence of oxygen to form nitrogen and water.

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

(iii) Basic nature: Ammonia is a Lewis base, accepting proton to form ammonium ion as it has tendency to donate an electron pair.

It forms salts with acids.

$$\begin{array}{ccc} NH_3 + HCl & \longrightarrow & NH_4Cl^* \\ & \text{Ammonium chloride} \\ & \text{Thick white} \\ & \text{fumes} \end{array}$$
 
$$2NH_3 + H_2SO_4 & \longrightarrow & (NH_4)_2SO_4 \\ & \text{Ammonium sulphate} \end{array}$$

Ammonia dissolves in water, its solution in water is a weak base. The solution is described as aqueous ammonia. The reaction between ammonia and water produces relatively few ions; ammonia remains mostly in the molecular form. It's ionisation in water is represented as,

The relatively few ions present do not conduct electricity well and ammonia may thus be called a **weak base** or **weak electrolyte**.

The solution turns red litmus to blue and phenolphthalein pink.

(iv) Oxidation: It is oxidised to nitrogen when passed over heated CuO or PbO.

$$\begin{array}{l} 3\text{CuO} + 2\text{NH}_3 \longrightarrow 3\text{Cu} + \text{N}_2 + 3\text{H}_2\text{O} \\ 3\text{PbO} + 2\text{NH}_3 \longrightarrow 3\text{Pb} + \text{N}_2 + 3\text{H}_2\text{O} \end{array}$$

Both chlorine and bromine oxidise ammonia.

$$\begin{array}{c} 2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl \\ 6NH_3 + 6HCl \longrightarrow 6NH_4Cl \\ \hline \\ 8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl \\ (Excess) \end{array}$$

When chlorine is in excess an explosive substance nitrogen trichloride is formed.

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

Iodine flakes when rubbed with liquor ammonia form a dark brown precipitate of ammoniated nitrogen iodide which explodes readily on drying.

$$2NH_3 + 3I_2 \longrightarrow NH_3 \cdot NI_3 + 3HI$$

Hypochlorites and hypobromites oxidise ammonia to nitrogen.  $2NH_3 + 3NaClO \longrightarrow N_2 + 3NaCl + 3H_2O$ 

The oxidation of ammonia with bleaching powder occurs on warming.

$$3CaOCl_2 + 2NH_3 \longrightarrow 3CaCl_2 + N_2 + 3H_2O$$

Thus, ammonia acts as a reducing agent.

The restricted oxidation of  $NH_3$  can be done with air, when the mixture is passed over heated platinum gauze at 700-800°C.

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$$

This is the Ostwald's process and used for the manufacture of HNO<sub>3</sub>.

(v) Formation of amides: When dry ammonia is passed over heated sodium or potassium, amides are formed with evolution of hydrogen.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2$$

(vi) Reactions of aqueous ammonia: Many metal hydroxides are formed which may be precipitated or remain dissolved in the form of complex compound in excess of  $NH_4OH$ .

$$FeCl_{3} + 3NH_{4}OH \longrightarrow Fe(OH)_{3} + 3NH_{4}Cl$$

$$ppt.$$

$$AlCl_{3} + 3NH_{4}OH \longrightarrow Al(OH)_{3} + 3NH_{4}Cl$$

$$ppt.$$

$$CrCl_{3} + 3NH_{4}OH \longrightarrow Cr(OH)_{3} + 3NH_{4}Cl$$

$$ppt.$$

$$CuSO_{4} + 2NH_{4}OH \longrightarrow Cu(OH)_{2} + (NH_{4})_{2}SO_{4}$$

$$Blue ppt.$$

$$\begin{array}{c} Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O \\ & \text{Tetramine copper} \\ & \text{sulphate} \\ & \text{(Deep blue soln.)} \end{array}$$

$$\begin{array}{c} CdSO_4 + 4NH_4OH \longrightarrow [Cd(NH_3)_4]SO_4 + 4H_2O \\ \hline Cadmium \ tetramine \\ sulphate \\ (Colourless \ soln.) \end{array}$$

$$\begin{array}{c} AgNO_3 + NH_4OH \longrightarrow AgOH + NH_4NO_3 \\ & \text{White ppt.} \end{array}$$

$$AgOH + 2NH_4OH \longrightarrow [Ag(NH_3)_2]OH + 2H_2O$$
  
Soluble

AgCl also dissolves in NH<sub>4</sub>OH solution.

$$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$$
Diamine silver chloride
$$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)_2SO_4$$

$$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)_2SO_4$$

$$Zn(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \longrightarrow$$

 $[Zn(NH_3)_4]SO_4 + 4H_2O$ Tetramine zinc sulphate

(Soluble) Colourless

Nickel salt first gives a green precipitate which dissolves in excess of NH<sub>4</sub>OH.

$$NiCl_2 + 2NH_4OH \longrightarrow Ni(OH)_2 + 2NH_4Cl$$

$$Ni(OH)_2 + 2NH_4Cl + 4NH_4OH \longrightarrow [Ni(NH_3)_6]Cl_2 + 6H_2O$$

It forms a white precipitate with mercuric chloride.

$$\begin{array}{c} HgCl_2 + 2NH_4OH \longrightarrow HgNH_2Cl + NH_4Cl + 2H_2O \\ \text{Amido mercuric} \\ \text{chloride} \end{array}$$

It forms a grey precipitate with mercurous chloride.

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underbrace{Hg + HgNH_2Cl}_{Grev} + NH_4Cl + 2H_2O$$

**(vii) Reaction with Nessler's reagent:** A reddish brown ppt. is formed.

$$2KI + HgCl_2 \longrightarrow HgI_2 + 2KCl$$

$$2KI + HgI_2 \longrightarrow K_2HgI_4$$

Alkaline solution of K<sub>2</sub>HgI<sub>4</sub> is called Nessler's reagent. This gives brown ppt. with NH<sub>3</sub> called iodide of Millon's base.

$$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow H_2NHgOHgI + 7KI + 2H_2O$$
Brown ppt.

(viii) Reaction with  $CO_2$ : When gaseous  $CO_2$  is reacted with liquid  $NH_3$  at 453-473 K under pressure of 220 atmospheres, it first forms ammonium carbamate which decomposes to give urea.

$$2NH_3 + CO_2 \longrightarrow NH_2COONH_4 \longrightarrow NH_2CONH_2 + H_2O$$
Ammonium carbamate Urea

(ix) Reaction with sodium hypochlorite: When a strong aqueous solution of ammonia is boiled with sodium hypochlorite in presence of glue, hydrazine is formed.

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$
  
 $NH_2Cl + NH_3 \longrightarrow NH_2 \cdot NH_2 + HCl$   
Chloramine Hydrazine

Hydrazine produced may be decomposed by chloramine into  $N_2$ .

$$2NH_2Cl + NH_2 \cdot NH_2 \longrightarrow N_2 + 2NH_4Cl$$

(x) Liquid ammonia as a solvent: Ammonia like water undergoes self ionisation in liquid state.

$$2NH_3 \Longrightarrow NH_4^+ + NH_2^-$$
$$2H_2O \Longrightarrow H_3O^+ + OH^-$$

Liquid ammonia is, thus, used for carrying out many reactions of polar compounds in non-aqueous medium.

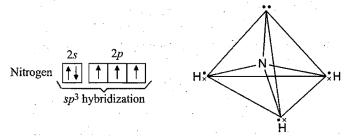
#### Uses:

- (i) Liquid ammonia is used in refrigeration on account of its large heat of evaporation.
  - (ii) Ammonia is used for making artificial silk.
- (iii) Ammonia is also the starting compound for the preparation of most of the other nitrogen compounds. Ammonia is used for the manufacture of nitric acid (Ostwald's process), sodium bicarbonate (Solvay process) and ammonium compounds. Ammonium sulphate, ammonium calcium phosphate, ammonium calcium nitrate, etc., are used as fertilizers. Ammonium nitrate is used in certain explosives. Ammonia is also used in the manufacture of urea, NH<sub>2</sub>CONH<sub>2</sub> which is an excellent fertilizer of nitrogen and is used in the manufacture of urea-formaldehyde plastics.
- (iv) Ammonia is used in the form of ammonium hydroxide (aq. solution) in the laboratory in qualitative and quantitative analysis.
- (v) Liquid hydrogen is not safe to transport in cylinders. Ammonia can be easily liquefied and transported safely in cylinders. Ammonia can be decomposed into hydrogen and nitrogen by passing over heated metallic catalysts. Thus, ammonia is the source for the production of hydrogen at any destination.
- (vi) It is used as a cleansing agent for removing grease.
   Tests of ammonia: (i) It is identified by its characteristic odour.
- (ii) It turns moist red litmus paper blue and moist turmeric paper brown.
- (iii) With a drop of HCl, it forms thick white fumes of ammonium chloride.
- (iv) With Nessler's reagent, it forms a reddish brown precipitate or colouration.
- (v) Ammonia gas when passed through copper sulphate solution gives a deep blue colour.
  - (vi) It gives a yellow precipitate with chloroplatinic acid.

$$\begin{array}{ccc} 2NH_3 \, + \, H_2PtCl_6 & \longrightarrow & (NH_4)_2PtCl_6 \\ & & \text{Ammonium } & \text{chloroplatinate} \\ & & & (Yellow) \end{array}$$

**Structure:** Ammonia is a covalent molecule. Three hydrogen atoms are linked to nitrogen by single covalent bonds. Its simple electronic structure may be represented as:

The formation of ammonia molecule involves sp<sup>3</sup> hybridization of nitrogen atom giving rise to four hybrid orbitals directed towards the four corners of a tetrahedron.



Three hybrid orbitals having single electron each form sigma bonds with three hydrogen atoms and the fourth hybrid orbital contains one pair of electrons. On account of the presence of this lone pair of electrons, the molecule gets distorted and acquires a *pyramidal structure*. The bond angle

N is not 
$$109^{\circ}28'$$
 but it is about  $107.5^{\circ}$ .

#### Ammonium compounds

The compounds having NH<sub>4</sub><sup>+</sup> ions are called ammonium compounds. Some of the general characteristics of these compounds are described below:

(a) These are generally white crystalline solids, dissolve in water and are strong electrolytes. Salts of strong acids give acidic solutions.

$$NH_{4}CI + H_{2}O \Longrightarrow NH_{4}OH + HCI$$

- (b) They resemble the salts of potassium and rubidium in solubility and structure since the three ions are of comparable radii :  $NH_4^+ = 148 \text{ pm}$ ,  $K^+ = 133 \text{ pm}$ ,  $Rb^+ = 148 \text{ pm}$ .
  - (c) When heated with alkali, they evolve ammonia.

$$NH_4Cl + NaOH \longrightarrow NH_3 + NaCl + H_2O$$
or
$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$$

- (d) Ammonium compounds with Nessler's reagent give a reddish brown precipitate or colouration.
- (e) Many ammonium compounds volatilise with dissociation around 300°C. For example,

$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$$
  
 $NH_4NO_3(s) \longrightarrow NH_3(g) + HNO_3(g)$ 

(f) Salts that contain oxidising anion first decompose giving NH<sub>3</sub> and then NH<sub>3</sub> is oxidised to N<sub>2</sub> or N<sub>2</sub>O or both on heating.

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

[Note: The reaction of ammonium dichromate is often referred to as the "Volcano" reaction. A source of heat, such as lighted match, will cause the orange crystals to decompose, producing sparks and a large volume of dark green chromic oxide, Cr<sub>2</sub>O<sub>3</sub>. This reaction should not be carried in open.]

#### Some of the important ammonium compounds are:

(i) Ammonium hydroxide, NH<sub>4</sub>OH: It is the aqueous solution of ammonia and behaves as a weak base.

$$NH_3 + H_2O \Longrightarrow NH_4OH \Longrightarrow NH_4^+ + OH^-$$

(ii) Ammonium chloride, NH<sub>4</sub>Cl: This ammonium compound is also known as salammoniac. It is obtained by reacting NH<sub>3</sub> with HCl.

It is a white crystalline solid, highly soluble in water. It is a volatile salt and decomposes at high temperatures into ammonia and hydrochloric acid gas. These two gases again combine on cooling.

$$NH_4CI \Longrightarrow NH_3 + HCI$$

The main uses of ammonium chloride are in soldering and tinning, in making of dry cells, in dyeing and calicoprinting and in medicine. It is also used as a laboratory reagent.

(iii) Ammonium sulphate, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>: It is known in India as sindri fertilizer. It can be obtained by absorbing NH<sub>3</sub> in 60% H<sub>2</sub>SO<sub>4</sub>.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

It is a colourless crystalline solid and highly soluble in water. It is used as a nitrogen fertilizer and a reagent in the laboratory.

(iv) Ammonium nitrate, NH<sub>4</sub>NO<sub>3</sub>: It is prepared by passing ammonia gas in 60% nitric acid.

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

It is a colourless, deliquescent solid. It is very soluble in water. On gentle heating it decomposes and evolves nitrous oxide.

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

This is an explosive solid. On rapid heating it explodes.

$$2NH_4NO_3 \longrightarrow 2N_2 + O_2 + 4H_2O$$

It is mainly used for making explosives such as amatol and ammonal.

**Amatol:**  $80\%NH_4NO_3 + 20\% T.N.T.$ 

**Ammonal:**  $NH_4NO_3 + Al$  powder (small quantity)

It is also used as a fertilizer. For this purpose, it is mixed with other substances, e.g.,

Leuna saltpetre  $NH_4NO_3 + (NH_4)_2SO_4$ 

Nitro chalk NH<sub>4</sub>NO<sub>3</sub> + CaCO<sub>3</sub>

#### 2. Hydrazine or Diamide, NH<sub>2</sub>·NH<sub>2</sub> or N<sub>2</sub>H<sub>4</sub>

This is another hydride of nitrogen. It is prepared by following methods:

(i) Raschig's method: A strong aqueous solution of ammonia is boiled with sodium hypochlorite in presence of a little glue.

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$
 $NH_2Cl + NH_3 \longrightarrow NH_2\cdot NH_2 + HCl$ 
Chloramine Hydrazine

 $2NH_3 + NaOCl \longrightarrow NH_2 \cdot NH_2 + NaCl + H_2O$ 

[Hydrazine produced may be decomposed by chloramine to  $N_2$ .

$$2NH_2Cl + N_2H_4 \longrightarrow 2NH_4Cl + N_2$$

The function of glue is to prevent this reaction. The yield is about 60-70%.]

Recovery of hydrazine from the above solution is made in the following manner:

$$\begin{array}{c} \text{Solution} \xrightarrow{H_2SO_4} N_2H_5 \cdot \text{HSO}_4 \xrightarrow{NaOH} N_2H_4 \cdot H_2O \xrightarrow{Distilled} \\ \text{Sparingly soluble} & \text{Hydrazine} \\ \text{hydrate} \end{array}$$

NH<sub>2</sub>·NH<sub>2</sub> Hydrazine

(ii) Hydrazine may also be obtained by treating a solution of K<sub>2</sub>SO<sub>3</sub> saturated with NO with sodium amalgam (reduction of NO).

$$K_2SO_3\cdot N_2O_2 + 6H \longrightarrow K_2SO_4 + N_2H_4 + H_2O$$

Recovery is made from the solution as described above. It is a colourless furning liquid. It is miscible with water in all proportions. It is soluble in alcohol.

It acts as diacid base. Thus, it forms two series of salts.

NH<sub>2</sub>·NH<sub>3</sub>Cl ClH<sub>3</sub>N·NH<sub>3</sub>Cl Hydrazine Hydrazine monochloride dichloride

It burns in air liberating huge amount of energy. The alkyl derivatives of hydrazine are used these days as potential rocket fuels. It reacts with nitrous acid to give hydrazoic acid, N<sub>3</sub>H.

$$N_2H_4 + HNO_2 \longrightarrow N_3H + 2H_2O$$

Hydrazine and its salts act as powerful reducing agents.

$$\begin{array}{c} \text{PtCl}_4 + \text{N}_2\text{H}_4 \longrightarrow \text{Pt} + \text{N}_2 + 4\text{HCl} \\ 4\text{AgNO}_3 + \text{N}_2\text{H}_4 \longrightarrow 4\text{Ag} + \text{N}_2 + 4\text{HNO}_3 \\ 4\text{AuCl}_3 + 3\text{N}_2\text{H}_4 \longrightarrow 4\text{Au} + 3\text{N}_2 + 12\text{HCl} \end{array}$$

It reduces Fehling's solution to red cuprous oxide, iodates to iodides and decolourises acidified KMnO<sub>4</sub> solution. It is used as a fuel for rockets, reducing agent and a reagent in organic chemistry.

Structure  $N = \frac{110^{\circ}}{1.47\text{\AA}} \text{N} = 110^{\circ}$ 

#### ■ 3. Hydrazoic Acid, N<sub>3</sub>H

It is the third hydride of nitrogen. It is an acid while other hydrides, NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> are bases. It is prepared by the action of nitrous acid on hydrazine.

$$NH_2 \cdot NH_2 + HNO_2 \longrightarrow N_3H + 2H_2O$$

It is also formed in the form of sodium salt by passing nitrous oxide on sodamide.

Pure hydrazoic acid is a colourless liquid. It is volatile and has very bad odour. It is poisonous in nature. It explodes violently when struck or heated. It is soluble in water and alcohol. It is slightly stronger acid. It dissolves many metals forming azides.

$$2N_3H + Mg \longrightarrow Mg(N_3)_2 + H_2$$

Silver, lead and mercurous azides are formed by reacting their soluble salts with N<sub>3</sub>H.

$$AgNO_3 + N_3H \longrightarrow AgN_3 + HNO_3$$

These azides explode violently when struck (used as detonators).

It reduces acidified KMnO<sub>4</sub>, nitrous acid, etc.

$$2N_3H + O \longrightarrow 3N_2 + H_2O$$
  
 $N_3H + HNO_2 \longrightarrow N_2 + N_2O + H_2O$ 

It oxidises HCl into Cl<sub>2</sub>.

$$N_3H + 2HCl \longrightarrow N_2 + NH_3 + Cl_2$$

Hydrazoic acid is a resonance hybrid.

$$\mathbf{H} - \mathbf{N} = \mathbf{N} = \mathbf{N} : \longleftrightarrow \mathbf{H} - \mathbf{N} : \longrightarrow \mathbf{N} = \mathbf{N}$$

#### 4. Oxides of Nitrogen

Nitrogen forms a number of oxides. The well known oxides of nitrogen are:

(i) Nitrous oxide,  $N_2O$ , (ii) Nitric oxide, NO, (iii) Nitrogen trioxide,  $N_2O_3$ , (iv) Nitrogen dioxide or Dinitrogen tetroxide,  $NO_2$  or  $N_2O_4$  and (v) Nitrogen pentoxide,  $N_2O_5$ . Nitrous oxide is nontoxic in small amounts but all the other nitrogen oxides are highly toxic.

# (I) Dinitrogen Oxide or Nitrous Oxide, N<sub>2</sub>O or Laughing Gas (Oxidation number +1)

**Preparation:** It can be prepared by heating ammonium nitrate or a mixture of sodium nitrate and ammonium sulphate.

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

$$2NaNO_3 + (NH_4)_2SO_4 \longrightarrow 2NH_4NO_3 + Na_2SO_4$$

$$\downarrow \qquad \qquad \downarrow$$

$$2N_2O + 4H_2O$$

The mixture consists of three parts ammonium sulphate and four parts sodium nitrate. It is heated carefully below 240°C. The evolved gas is collected over hot water as it is fairly soluble in cold water. It is usually contaminated with nitric oxide (NO), ammonia (NH<sub>3</sub>) and water vapour. The gas is passed through ferrous sulphate solution to remove nitric oxide and through concentrated sulphuric acid to remove ammonia and water vapour.

$$\begin{array}{cccc} FeSO_4 + NO & \longrightarrow & FeSO_4 \cdot NO \\ & & Addition \ product \\ H_2SO_4 + 2NH_3 & \longrightarrow & (NH_4)_2SO_4 \\ & & & Ammonium \ sulphate \\ \end{array}$$

The following reactions can also be used to prepare nitrous oxide.

(a) By the action of cold and dilute nitric acid on zinc metal.

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

(b) By reducing nitric acid with stannous chloride and hydrochloric acid.

$$4SnCl_2 + 8HCl + 2HNO_3 \longrightarrow 4SnCl_4 + N_2O + 5H_2O$$

(c) By reducing nitric oxide with sulphur dioxide.

$$2NO + SO_2 + H_2O \longrightarrow H_2SO_4 + N_2O$$

(d) By heating the mixture of hydroxylamine hydrochloride and sodium nitrite (1 : 1).

$$NH_2OH \cdot HCl + NaNO_2 \longrightarrow N_2O + NaCl + 2H_2O$$

**Properties:** (a) It is a colourless, tasteless gas with a pleasant and sweet odour.

- (b) When inhaled in moderate quantity, it produces hysterical laughter, hence named as **laughing gas.** However, when inhaled for long, it produces insensibility and may prove fatal too.
  - (c) It is heavier than air.
- (d) It is fairly soluble in cold water but not in hot water. It dissolves readily in fats and is tasteless and nontoxic in small amounts.

The solution in water is neutral in nature. This is probably due to the following equilibrium which lies in the left hand side.

$$N_2O + H_2O \Longrightarrow H_2N_2O_2 + H_2O \Longrightarrow H_2O_2 + H_2O_2 +$$

The oxide may be taken as an anhydride of hyponitrous acid. However, the acid is not obtained by dissolving  $N_2O$  in water.

- (e) It is neutral to litmus.
- (f) It does not burn but supports combustion. The burning material decomposes nitrous oxide into nitrogen and oxygen. The oxygen then helps in the burning.

$$2N_2O \xrightarrow{520-900^{\circ}C} 2N_2 + O_2$$

It supports combustion of sulphur, phosphorus, magnesium, sodium, candle and a splinter.

$$S + 2N_2O \longrightarrow SO_2 + 2N_2$$

$$4P + 10N_2O \longrightarrow 2P_2O_5 + 10N_2$$

$$Mg + N_2O \longrightarrow MgO + N_2$$

$$2Na + N_2O \longrightarrow Na_2O + N_2$$

(g) It is decomposed by red hot copper.

$$Cu + N_2O \longrightarrow CuO + N_2$$

(h) A mixture of hydrogen and nitrous oxide (equal volumes) explodes with violence.

$$N_2O + H_2 \longrightarrow N_2 + H_2O$$

(i) It forms sodium azide on reaction with NaNH<sub>2</sub> (sodamide).

$$NaNH_2 + N_2O \longrightarrow NaN_3 + H_2O$$
  
 $NaNH_2 + H_2O \longrightarrow NaOH + NH_3$ 

$$\frac{}{2\text{NaNH}_2 + \text{N}_2\text{O} \longrightarrow \text{NaN}_3 + \text{NaOH} + \text{NH}_3}$$

Uses: (i) A mixture of nitrous oxide and oxygen is used as an dental anaesthetic and other minor surgical operations.

(ii) It is sometime used as a foaming agent and as a propellant gas for whipped-cream dispensers. The gas dissolves in cream under pressure. When the cream is dispersed, the gas bubbles out, forming a foam.

**Structure:** N<sub>2</sub>O is linear and unsymmetrical molecule. It is considered as a resonance hybrid of the following two structures:

$$: \stackrel{\cdot}{N} \xrightarrow{\sigma} \stackrel{+}{N} \xrightarrow{\sigma} \stackrel{\cdot}{O} : \longleftrightarrow : \stackrel{\cdot}{N} \xrightarrow{\frac{\sigma}{2\pi}} \stackrel{+}{N} \xrightarrow{\sigma} \stackrel{\cdot}{O} :$$

The bond length between N-N is 113 pm and between N-O is 119 pm.

It has a very small value of dipole moment (0.116 D).

Tests: (i) It is a gas with pleasant odour.

- (ii) It supports the combustion of glowing splinter.
- (iii) It does not form brown fumes with nitric oxide.

#### (II) Nitric Oxide, NO

(Oxidation number +2)

Preparation: (a) By the action of dilute nitric acid on copper (Lab. method).

Copper chips are taken in a Woulfe-bottle and some water is added. Concentrated nitric acid is poured through the thistle funnel and the nitric oxide liberated is collected over water.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

The liberated gas may contain NO<sub>2</sub> and N<sub>2</sub>O. These are separated by passing the mixture through ferrous sulphate solution. NO forms a dark brown nitroso-ferrous sulphate. When this solution is heated, pure nitric oxide is liberated.

$$FeSO_4 + NO \xrightarrow{\text{(Impure gas)}} FeSO_4 \cdot NO \xrightarrow{\text{Heat}} FeSO_4 + NO \xrightarrow{\text{(Pure gas)}}$$

(b) A pure sample of nitric oxide is obtained when a mixture of KNO<sub>3</sub>, FeSO<sub>4</sub> and dilute H<sub>2</sub>SO<sub>4</sub> is heated. This is also a laboratory method.

$$2KNO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_3$$

$$2HNO_3 \longrightarrow H_2O + 2NO + 3O$$

$$[2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 3$$

 $2KNO_3+6FeSO_4+4H_2SO_4 \rightarrow K_2SO_4+3Fe_2(SO_4)_3+2NO+4H_2O$ 

- (c) Nitric oxide is the first product obtained from the following two processes during the manufacture of nitric acid.
- (i) Electric arc process: By passing air through an electric arc, nitrogen and oxygen of the air combine together to form nitric oxide.

$$N_2 + O_2 \stackrel{\text{Electric arc}}{\longleftarrow} 2NO$$

(ii) Ostwald's process: By restricted oxidation of ammonia with air in presence of platinum gauze catalyst at 750°C, nitric oxide is formed.

$$4NH_3 + 5O_2 \xrightarrow{Pt. \text{ gauze}} 4NO + 6H_2O$$

Properties: (a) It is a colourless gas, slightly heavier than air.

- (b) It is sparingly soluble in water.
- (c) It is liquefied with difficulty under high pressure and low temperature (-151°C).
- (d) It is paramagnetic indicating the presence of unpaired electron in the molecule.
  - (e) It is neutral to litmus.
- (f) It at once reacts with oxygen to give brown fumes of nitrogen dioxide.

$$2NO + O_2 \longrightarrow 2NO_2$$

(g) It is stable oxide. It decomposes into nitrogen and oxygenwhen heated at 800°C.

$$2NO \xrightarrow{800^{\circ}C} N_2 + O_2$$

(h) It is combustible and supports combustion of boiling sulphur and burning phosphorus.

$$S + 2NO \longrightarrow SO_2 + N_2$$

(i) It dissolves in cold ferrous sulphate solution by forming a hydrated nitrosyl complex.

In the complex [Fe(H<sub>2</sub>O)<sub>5</sub>NO]SO<sub>4</sub>, iron is assumed to exhibit Fe<sup>2+</sup> state, but from magnetic moment measurements it is observed that iron exhibits +1 oxidation state instead of +2. In this complex, 'NO' exhibits +1 oxidation state.

(j) It is oxidised to nitric acid by oxidising agents like acidified KMnO<sub>4</sub> or hypochlorous acid. Thus, it acts as a reducing agent.

$$[2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O] \times 3$$

$$[NO + O \longrightarrow NO_2] \times 15$$

$$[3NO_2 + H_2O \longrightarrow 2HNO_3 + NO] \times 5$$

$$6KMnO_4 + 9H_2SO_4 + 10NO \longrightarrow 3K_2SO_4 + 6MnSO_4 + 10HNO_3 + 4H_2O$$

$$[\text{HCIO} \longrightarrow \text{HCI} + \text{O}] \times 3$$

$$[\text{NO} + \text{O} \longrightarrow \text{NO}_2] \times 3$$

$$3\text{NO}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_3 + \text{NO}$$

$$3HClO + 2NO + H_2O \longrightarrow 2HNO_3 + 3HCl$$
  
 $HNO_3$  oxidises nitric oxide into  $NO_2$ .

$$2HNO_3 + NO \longrightarrow H_2O + 3NO_2$$

(k) It acts as an oxidising agent. It oxidises  $SO_2$  to  $H_2SO_4$  and  $H_2S$  to S.

$$SO_2 + 2NO + H_2O \longrightarrow H_2SO_4 + N_2O$$
  
 $H_2S + 2NO \longrightarrow H_2O + S + N_2O$ 

When exploded with hydrogen, it liberates nitrogen.

$$2H_2 + 2NO \longrightarrow 2H_2O + N_2$$

However, when a mixture of hydrogen and nitric oxide is passed over platinum black, ammonia is formed.

$$2NO + 5H_2 \longrightarrow 2NH_3 + 2H_2O$$

Stannous chloride reduces nitric oxide to hydroxylamine.

$$[SnCl2 + 2HCl \longrightarrow SnCl4 + 2H] \times 3$$

$$2NO + 6H \longrightarrow 2NH2OH$$

$$3\text{SnCl}_2 + 6\text{HCl} + 2\text{NO} \longrightarrow 3\text{SnCl}_4 + 2\text{NH}_2\text{OH}$$

(l) Nitric oxide directly combines with halogens (fluorine, chlorine, bromine) to form corresponding nitrosyl halides.

2NO + 
$$X_2 \longrightarrow 2NOX$$
  
(F<sub>2</sub>, Cl<sub>2</sub> or Br<sub>2</sub>) Nitrosyl halide

Uses: (i) In the manufacture of nitric acid.

- (ii) As a catalyst in lead chamber process for the manufacture of sulphuric acid.
- (iii) In the detection of oxygen to distinguish it from nitrous oxide.

**Structure:** The molecule NO has eleven valency electrons and it is impossible for all of them to be paired. Hence, the molecule contains an odd electron which makes the gaseous nitric oxide as paramagnetic.

The structure is represented as a resonance hybrid.

$$: \overset{\scriptscriptstyle +}{N} = \overset{\scriptstyle -}{0} : \overset{\scriptstyle -}{\longleftrightarrow} : \overset{\scriptstyle -}{N} = \overset{\scriptstyle -}{0} : \overset{\scriptstyle -}{\longleftrightarrow} : \overset{\scriptstyle -}{N} = \overset{\scriptstyle -}{0} :$$

In the liquid and solid states, NO is known to form a loose dimer,  $N_2O_2$ . In this form, it is diamagnetic.

Note: The electron configuration of NO is:

$$KK(\sigma^2 s)^2 (\sigma^2 s)^2 (\sigma^2 p_z)^2 (\pi^2 p_x)^2 (\pi^2 p_x)^4 (\pi^2 p_x)^4$$

The  $\overset{*}{\pi}$  electron is lost easily to give nitrosonium ion, NO<sup>+</sup> which forms many salts. NO<sup>+</sup> can be obtained by reacting N<sub>2</sub>O<sub>3</sub> with H<sub>2</sub>SO<sub>4</sub>.

$$N_2O_3 + 3H_2SO_4 \longrightarrow 2NO^+ + 3HSO_4^- + H_3O^+$$
  
From solution, NOHSO<sub>4</sub> is isolated.

# (III) Dinitrogen Trioxide, N<sub>2</sub>O<sub>3</sub> (Oxidation number +3)

This oxide is also called **nitrogen sesquioxide** or **nitrous** anhydride.

**Preparation:** It is obtained by the reduction of nitric acid with arsenious oxide.

$$2HNO_3 \longrightarrow H_2O + N_2O_3 + 2O$$

$$As_2O_3 + 2O \longrightarrow As_2O_5$$

$$As_2O_5 + 3H_2O \longrightarrow 2H_3AsO_4$$

$$As_2O_3 + 2HNO_3 + 2H_2O \longrightarrow 2H_3AsO_4 + N_2O_3$$

It is known in pure state in solid form at very low temperature. In the vapour state, it is present as an equimolecular mixture of NO and NO<sub>2</sub>. The mixture of NO and NO<sub>2</sub> may be obtained by the action of 6N nitric acid on copper.

$$2\text{Cu} + 6\text{HNO}_3 \longrightarrow 2\text{Cu}(\text{NO}_3)_2 + \underbrace{\text{NO} + \text{NO}_2}_{\text{N}_2\text{O}_3} + 3\text{H}_2\text{O}$$

**Properties:** (a) It condenses to a blue coloured liquid at -30°C. The liquid when warmed at room temperature, decomposes to a mixture of NO and NO<sub>2</sub> (brown coloured).

$$\begin{array}{c} N_2O_3 \\ \text{Blue coloured liquid} \end{array} \xrightarrow{\text{Room temp.}} \underbrace{\begin{array}{c} NO+NO_2 \\ \text{Brown coloured gas} \end{array} }_{\text{Brown coloured gas}}$$

(b) It is an acidic oxide. It forms nitrous acid with water and hence the name nitrous anhydride.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

The oxide combines with caustic alkali forming corresponding nitrite.

$$2NaOH + N_2O_3 \longrightarrow 2NaNO_2 + H_2O$$

**Structure:** Since the oxide is unstable in liquid and gaseous states and decomposes into NO and NO<sub>2</sub>, it may be assumed that it has the following electronic structure:

$$: O: \stackrel{\times}{\times} \stackrel{\times}{N} \times : O: \stackrel{\times}{\times} \stackrel{\times}{\times} : O:$$
 or  $O=N-O-N=O$ 

The structure is supported by its diamagnetic behaviour. Structure of  $N_2O_3$  is of two forms:

# (IV) Nitrogen Dioxide, NO<sub>2</sub> or Dinitrogen Tetroxide, N<sub>2</sub>O<sub>4</sub> (Oxidation number +4)

This oxide exists as  $NO_2$  in gaseous state while at low temperature, it exists as a dimer  $N_2O_4$  (solid state).

$$\begin{array}{ccc} 2NO_2 & \xrightarrow{-11^{\circ}C} & N_2O_4 \\ \text{Brown gas} & & \text{Colourless solid} \end{array}$$

**Preparation:** It is prepared in the laboratory either by heating nitrates of heavy metals or by the action of concentrated nitric acid on metals like copper, silver, lead, etc.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

The mixture of nitrogen dioxide and oxygen is passed through a U-tube cooled by freezing mixture. Nitrogen

dioxide condenses to a pale yellow liquid while oxygen escapes.

Cu + 4HNO<sub>3</sub>  $\longrightarrow$  Cu(NO<sub>3</sub>)<sub>2</sub> + 2NO<sub>2</sub> + 2H<sub>2</sub>O It is also obtained by air oxidation of nitric oxide.

$$2NO + O_2 \longrightarrow 2NO_2$$

**Properties:** (a) It is a brown coloured gas with pungent odour. Above 140°C, it is 100% NO<sub>2</sub>. The liquid as well as solid is entirely  $N_2O_4$  (dimer) at low temperature. The liquid boils at 22°C and solid melts at -11°C.

(b) It decomposes completely into nitric oxide and oxygen at 620°C.

$$2NO_2 \xrightarrow{620^{\circ}C} \underbrace{2NO + O_2}_{Gaseous \ mixture}$$

$$\underbrace{Colourless}_{(Colourless)}$$

(c) When reacted with cold water, it forms a mixture of nitrous acid and nitric acid.

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

On account of this, it is known as **mixed anhydride** of these two acids. However, with an excess of warm water it forms nitric acid and nitric oxide.

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

(d) When absorbed by alkalies, nitrites and nitrates are formed.

$$2NO_2 + 2NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

(e) It acts as an oxidising agent. It oxidises metals like sodium, potassium, mercury, tin, copper, etc.

$$NO_2 + 2Na \longrightarrow Na_2O + NO$$
  
 $NO_2 + 2Cu \longrightarrow Cu_2O + NO$ 

Non-metals like carbon, sulphur, phosphorus when burnt in its atmosphere, are converted into corresponding oxides.

$$5NO_2 + 2P \longrightarrow P_2O_5 + 5NO$$
  
 $2NO_2 + S \longrightarrow SO_2 + 2NO$   
 $2NO_2 + C \longrightarrow CO_2 + 2NO$ 

It liberates iodine from KI and turns starch-iodide paper blue.

$$2KI + 2NO_2 \longrightarrow 2KNO_2 + I_2$$

In aqueous solution, it oxidises SO<sub>2</sub> to sulphuric acid.

$$SO_2 + H_2O + NO_2 \longrightarrow H_2SO_4 + NO$$

This reaction is used for the manufacture of H<sub>2</sub>SO<sub>4</sub> by lead chamber process.

H<sub>2</sub>S is oxidised to S and CO to CO<sub>2</sub>.

$$H_2S + NO_2 \longrightarrow H_2O + S + NO$$
  
 $CO + NO_2 \longrightarrow CO_2 + NO$ 

(f) It behaves also as a reducing agent. It reduces ozone to oxygen.

$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

It decolourises acidified KMnO<sub>4</sub> solution.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
  
 $10NO_2 + 5H_2O + 5O \longrightarrow 10HNO_3$ 

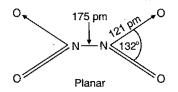
$$2KMnO_4 + 3H_2SO_4 + 10NO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 10HNO_3$$

**Uses:** (i) It is used for the manufacture of nitric acid. (ii) It is employed as a catalyst in the lead chamber process for the manufacture of sulphuric acid.

**Structure:** NO<sub>2</sub> molecule has V-shaped structure with O—N—O bond angle 132° and N—O bond length of about 119 pm which is intermediate between a single and a double bond. Hence, NO<sub>2</sub> is regarded as a resonance hybrid of the following two structures:



The molecule is an odd electron molecule. The paramagnetic behaviour of  $NO_2$  confirms this view. Due to possession of odd electron, it is coloured and has a tendency to polymerise to form a colourless dimer,  $N_2O_4$ . The dimer is planar in structure with N—N bond length 175 pm.



# (V) Dinitrogen or Nitrogen Pentoxide, N<sub>2</sub>O<sub>5</sub> (oxidation number +5)

This oxide is also known as nitric anhydride.

**Preparation:** It is prepared by distilling concentrated nitric acid with phosphorus pentoxide in a glass apparatus.

$$2HNO_3 \longrightarrow H_2O + N_2O_5$$

$$P_2O_5 + H_2O \longrightarrow 2HPO_3$$

$$P_2O_5 + 2HNO_3 \longrightarrow 2HPO_3 + N_2O_5$$

It is also prepared by the action of dry chlorine on solid silver nitrate at 95°C.

$$4AgNO_3 + 2Cl_2 \longrightarrow 4AgCl + 2N_2O_5 + O_2$$

**Properties:** (a) It is a white crystalline solid. The crystals melt at 30°C giving a yellow liquid which decomposes at 40°C to give brown NO<sub>2</sub>. The decomposition occurs with explosion.

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

(b) It is an acidic oxide. It reacts with water with hissing sound forming nitric acid.

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

On account of this, it is known as nitric anhydride. With alkalies it forms nitrates.

$$2NaOH + N_2O_5 \longrightarrow 2NaNO_3 + H_2O$$

(c) It acts as a strong oxidising agent. It affects organic substances such as cork, rubber, etc. It oxidises iodine readily into iodine pentoxide.

$$I_2 + 5N_2O_5 \longrightarrow I_2O_5 + 10NO_2$$

(d) With aqueous NaCl, the ionic reaction takes place.

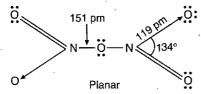
$$N_2O_5 + NaCl \longrightarrow NaNO_3 + NO_2Cl$$

The reaction proves that  $N_2O_5$  exists as ionic nitronium nitrate  $(NO_2^+ NO_3^-)$ .

(e) N<sub>2</sub>O<sub>5</sub> is decomposed by alkali metals.

$$N_2O_5 + Na \longrightarrow NaNO_3 + NO_2 \uparrow$$

**Structure:** In the gaseous state, it exists as a symmetrical molecule having the structure  $O_2N-O-NO_2$ . N-O-N bond is almost linear. It may be represented as:



X-ray studies suggest that solid  $N_2O_5$  is ionic in nature, *i.e.*, nitronium nitrate,  $NO_2^+$   $NO_3^-$ .

#### 5. Oxyacids of Nitrogen

Nitrogen forms a number of oxyacids. The most common and important oxyacids are:

(i) Nitrous acid, HNO2 and (ii) Nitric acid, HNO3.

#### (I) Nitrous Acid, HNO<sub>2</sub>

The free acid is unknown. It is known only in solution.

**Preparation:** Nitrous acid is unstable and is usually prepared when needed as an aqueous solution. A solution of nitrous acid can be prepared by acidifying solutions of nitrites with mineral acids.

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$$
  
 $KNO_2 + HCl \longrightarrow KCl + HNO_2$ 

Nitrates on heating with lead decompose to give nitrite.

$$NaNO_3 + Pb \xrightarrow{\Delta} NaNO_2 + PbO$$

An aqueous solution of the acid, free from any salt, can be prepared by treating barium nitrite with calculated amount of dilute sulphuric acid. Since the acid is very unstable, the reaction is carried out at low temperature (freezing mixture temperature). The insoluble barium sulphate is filtered off.

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HNO_2$$
Insoluble

A solution of nitrous acid may also be prepared by dissolving  $N_2O_3$  in water.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

**Properties:** (a) Aqueous solution of nitrous acid is pale blue. This is due to the presence of nitrogen trioxide,  $N_2O_3$ . The colour fades on standing for sometime.

(b) It is a weak acid and reacts with alkalies to form salts known as nitrites.

$$HNO_2 + NaOH \longrightarrow NaNO_2 + H_2O$$

(c) Auto-oxidation: The acid is unstable and even in cold solution, it undergoes auto-oxidation.

$$2HNO_2 \longrightarrow 2NO + H_2O + O$$

$$HNO_2 + O \longrightarrow HNO_3$$

$$3HNO_2 \longrightarrow 2NO + HNO_3 + H_2O$$

On heating, it decomposes into nitric oxide and nitrogen dioxide.

$$2HNO_2 \longrightarrow H_2O + N_2O_3$$

NO + NO<sub>2</sub>

(Brown)

(d) **Oxidising nature:** It acts as an oxidising agent due to ease with which it decomposes to give nascent oxygen. The potential equation when it acts as an oxidising agent is:

$$2HNO_2 \longrightarrow H_2O + 2NO + O$$

(i) Iodine is liberated from potassium iodide.

$$2KI + H_2SO_4 + 2HNO_2 \longrightarrow K_2SO_4 + 2NO + I_2 + 2H_2O$$

- (ii) Stannous chloride is oxidised to stannic chloride.
- $SnCl_2 + 2HCl + 2HNO_2 \longrightarrow SnCl_4 + 2NO + 2H_2O$

(iii) Sulphur dioxide is oxidised to sulphuric acid.  

$$SO_2 + 2HNO_2 \longrightarrow H_2SO_4 + 2NO$$

(iv) Sulphur is formed by oxidation of hydrogen sulphide.  $H_2S + 2HNO_2 \longrightarrow S + 2H_2O + 2NO$ 

(v) Actument retrous surplinate is oxidised to terms surplinate.  $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + 2\text{HNO}_2 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NO} + 2\text{H}_2\text{O}$ 

(vi) Sodium arsenite is oxidised to sodium arsenate.

$$Na_3AsO_3 + 2HNO_2 \longrightarrow Na_3AsO_4 + 2NO + H_2O$$

(e) **Reducing nature:** Nitrous acid acts as a reducing agent as it can be oxidised into nitric acid.

$$HNO_2 + O \longrightarrow HNO_3$$

(i) It reduces bromine to hydrobromic acid.

$$Br_2 + H_2O + HNO_2 \longrightarrow 2HBr + HNO_3$$

(ii) Acidified potassium permanganate is decolourised.

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 \longrightarrow$$

$$K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$$

(iii) Acidified potassium dichromate is reduced to chromic sulphate (green).

$$K_2Cr_2O_7 + 4H_2SO_4 + 3HNO_2 \longrightarrow$$
  
 $K_2SO_4 + Cr_2(SO_4)_3 + 3HNO_3 + 4H_2O_4$ 

(iv) Hydrogen peroxide is reduced to water.

$$H_2O_2 + HNO_2 \longrightarrow HNO_3 + H_2O$$

(f) **Reaction with ammonia:** It reacts with ammonia to form nitrogen and water.

$$NH_3 + HNO_2 \longrightarrow [NH_4NO_2] \longrightarrow N_2 + 2H_2O$$
Intermediate

(g) **Reaction with urea:** It decomposes urea and other aliphatic primary amines to nitrogen.

$$NH_2CONH_2 + 2HNO_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$$
Urea
 $C_2H_5NH_2 + HO \cdot NO \longrightarrow C_2H_5OH + N_2 + H_2O$ 

(h) Reaction with aniline and other aromatic amines: It forms diazo compounds with aromatic amines at low temperatures.

$$C_6H_5NH_2\cdot HCl + HNO_2 \longrightarrow C_6H_5N = NCl + 2H_2O$$
Aniline hydro-
chloride

Aniline hydro-
chloride

Chloride

**Uses:** (i) It is used in organic chemistry in the preparation of diazo compounds which are employed for making aniline dves.

- (ii) It is also used for the replacement of —NH<sub>2</sub> group by—OH group in aliphatic primary amines.
- (iii) In analytical chemistry, it is used both as an oxidising and reducing agent.

**Structure:** Since nitrous acid forms two types of organic derivatives, the nitrites (R—ONO) and nitro compounds (R—NO<sub>2</sub>), it is considered to be a tautomeric mixture of two forms.

Note: Possible oxidation state of nitrogen lies between +5 and -3. In HNO<sub>2</sub>; oxidation state of nitrogen is +3; the oxidation state may increase up to +5 and decrease up to -3. Thus, HNO<sub>2</sub> acts both as oxidising and reducing agent. On the other hand in HNO<sub>3</sub>, oxidation state of nitrogen is +5, thus, it acts only as oxidising agent (itself undergoing reduction till -3 oxidation state is achieved).

#### (II) Nitric Acid, HNO<sub>3</sub>

It was named **aqua fortis** (meaning strong water) by alchemists. Glauber obtained it by the action of sulphuric acid on nitre.

**Laboratory preparation:** It is prepared in the laboratory by heating a mixture of alkali nitrate and concentrated sulphuric acid in a glass retort as shown in Fig. 10.5.

$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$

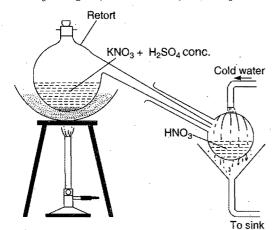


Fig. 10.5 Laboratory preparation of nitric acid

The vapours of nitric acid evolved are condensed in a glass receiver. The nitric acid thus obtained may contain oxides of nitrogen as impurity. The dissolved oxides of nitrogen are removed by redistillation or blowing a current of carbon dioxide through warm acid.

**Manufacture:** Nitric acid is of great commercial importance as it is needed in large amounts for the manufacture of explosives, fertilizers, dyes, drugs, etc. Before world war I, the only available method for the manufacture of nitric acid was the distilling of nitre with concentrated sulphuric acid. Now-a-days the following two processes are employed for the manufacture of nitric acid:

- (i) Birkeland and Eyde process or Arc process.
- (ii) Ostwald's process. This process is most recent.

#### (a) Birkeland and Eyde Process

**Principle:** The reaction between nitrogen and oxygen is reversible and endothermic in nature.

$$N_2 + O_2 \Longrightarrow 2NO -43,200$$
 calories

According to Le Chatelier's principle, the formation of nitric oxide is favoured by high temperature. The temperature is thus maintained about 3000°C by the use of an electric arc. The nitric oxide formed is immediately cooled to 1000°C as to prevent its decomposition. Nitric oxide further combines with oxygen to form nitrogen dioxide.

$$2NO + O_2 \longrightarrow 2NO_2$$

The vapours are then passed through water when nitric acid is produced.

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$
  
 $3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$ 

**Process:** Air is blown into an electric arc established between two water cooled copper electrodes and spread into a disc with the help of a strong magnetic field applied at right angles (Fig. 10.6). The electric arc produces a temperature of about 3000°C. Nitrogen and oxygen combine to form nitric oxide. The gases coming out of this furnace consists of 1.25 to 2% nitric oxide. These gases are cooled down quickly to 1000°C. The gases are further cooled to 150°C by passing through boiler pipes. The gases now enter the oxidation chamber where nitric oxide combines with oxygen and is oxidised to

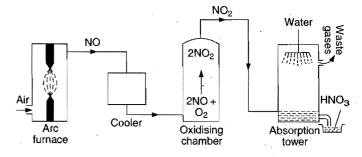


Fig. 10.6 Manufacture of nitric acid

nitrogen dioxide. Nitrogen dioxide thus produced is absorbed in water in the absorption tower (70 ft high and 20 ft in diameter) packed with quartz. The nitric acid in the first tower reaches a strength of 30 to 40% while in the succeeding towers, the strength is about 20, 10 and 5% respectively.

The utility of this method has declined gradually and today it is practically outdated because the yield in this process is very poor and the consumption of electrical power is high.

#### (b) Ostwald's Process (Modern Process)

**Principle:** The mixture of ammonia and air when passed over platinum gauze catalyst at 750–900°C, the ammonia is oxidised to nitric oxide (NO),

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O + 21,600$$
 calories

The reaction is exothermic and the heat of reaction maintains the temperature of the catalyst.

The nitric oxide is then oxidised to nitrogen dioxide, (NO<sub>2</sub>), by  $O_2$  from the air which is cooled to  $50^{\circ}$ C and absorbed in water. The resulting NO can be volatilized and recycled.

$$2NO + O_2 \longrightarrow 2NO_2$$
  
 $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$ 

**Process:** A mixture of dry ammonia and purified air (free from carbon dioxide and dust particles) in the ratio of 1:10 (by volume) is passed through the catalyst chamber containing platinum gauze (Fig. 10.7). The gauze is initially

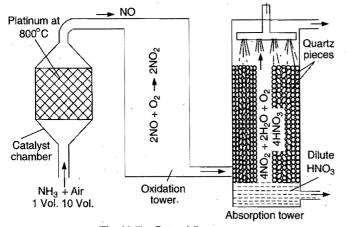


Fig.10.7 Ostwald's process

heated to about 800°C electrically. Subsequently, the temperature is maintained by heat of reaction. Ammonia is rapidly oxidised to nitric oxide. The yield varies from 90-95%.

The gases issuing from the converter are cooled and then mixed with air in large empty chamber known as oxidation chamber. Nitric oxide gets oxidised to nitrogen dioxide. Nitrogen dioxide is now absorbed in water in the absorption tower packed with broken quartz. The nitric oxide formed is again oxidised by oxygen and nitrogen dioxide is further absorbed by water. The total reaction thus is:

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

The concentration of acid produced is about 50-60%.

Concentration of nitric acid: Dilute nitric acid (50-60%) obtained in the above process is concentrated by distillation till a constant boiling mixture (b.pt. 121°C) is formed. This is ordinary concentrated nitric acid (sp. gr. 1.414) and its strength is 68%. More concentrated HNO<sub>3</sub> is produced by distilling the ordinary concentrated nitric acid with concentrated sulphuric acid. The distillate is 98% HNO<sub>3</sub> (sp. gr. 1.51). The cent per cent HNO<sub>3</sub> is obtained by cooling 98% HNO<sub>3</sub> in a freezing mixture. The colourless crystals (m.pt. -42°C) are melted to get 100% HNO<sub>3</sub>.

Fuming nitric acid: It contains dissolved NO<sub>2</sub> in concentrated nitric acid. It is brown in colour. Fuming acid is obtained by distilling concentrated HNO<sub>3</sub> with a little starch. Nitric acid is reduced by starch into NO<sub>2</sub> which dissolves in the remaining acid to form fuming nitric acid. Fuming nitric acid is a strong oxidising agent.

Physical properties: Anhydrous nitric acid is a colour-less fuming liquid having a pungent smell. Concentrated nitric acid is often pale yellow as a result of partial decomposition of the acid to NO<sub>2</sub>. It boils at 84.1°C and freezes at -42°C. It is soluble in water in all proportions. The aqueous solution containing about 68% of HNO<sub>3</sub> by weight forms a constant boiling mixture. This is the ordinary concentrated HNO<sub>3</sub> (sp. gr. 1.414). Nitric acid usually acquires yellow colour due to its decomposition by sunlight into NO<sub>2</sub>.

$$4\text{HNO}_3 \xrightarrow{\text{Sunlight}} 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2$$

The yellow colour of the acid can be removed by warming it to 60-80°C and bubbling dry air through it.

It has extremely corrosive action on the skin and causes painful sores.

#### **Chemical properties:**

(A) It is a very strong acid. It exhibits usual properties of acids. It reacts with basic oxides, carbonates, bicarbonates and hydroxides forming corresponding salts.

$$CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$
  
 $Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$   
 $NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$ 

#### (B) Oxidising nature

Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

$$2HNO_3 \longrightarrow H_2O + 2NO + 3O$$

- (i) Oxidation of non-metals: The nascent oxygen oxidises various non-metals to their corresponding highest oxyacids.
  - (1) Sulphur is oxidised to sulphuric acid.

$$[2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 3$$

$$S + 3O + H_2O \longrightarrow H_2SO_4$$

$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$
Conc. and hot

(2) Carbon is oxidised to carbonic acid.

$$[2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 2$$

$$C + 2O + H_2O \longrightarrow H_2CO_3$$

$$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + H_2O$$

(3) Phosphorus is oxidised to orthophosphoric acid.

$$[2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 5$$

$$2P + 5O + 3H_2O \longrightarrow 2H_3PO_4$$

$$2P + 10HNO_3 \longrightarrow 2H_3PO_4 + 10NO_2 + 2H_2O$$
Conc. and hot

(4) Iodine is oxidised to iodic acid.

$$[2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 5$$

$$I_2 + 5O + H_2O \longrightarrow 2HIO_3$$

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$
Conc. and hot

- (ii) Oxidation of metalloids: Metalloids like non-metals also form highest oxyacids.
  - (1) Arsenic is oxidised to arsenic acid.

$$[2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 5$$

$$2As + 5O + 3H_2O \longrightarrow 2H_3AsO_4$$

$$2As + 10HNO_3 \longrightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O$$
or
$$As + 5HNO_3 \longrightarrow H_3AsO_4 + 5NO_2 + H_2O$$
Conc. and hot

(2) Antimony is oxidised to antimonic acid.

Sb + 5HNO<sub>3</sub> 
$$\longrightarrow$$
 H<sub>3</sub>SbO<sub>4</sub> + 5NO<sub>2</sub> + H<sub>2</sub>O  
Conc. and hot

(3) Tin is oxidised to metastannic acid.

$$[2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 2$$

$$Sn + 2O + H_2O \longrightarrow H_2SnO_3$$

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

(iii) Oxidation of compounds: (1) Sulphur dioxide is oxidised to sulphuric acid.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

$$SO_2 + O + H_2O \longrightarrow H_2SO_4$$

$$SO_2 + 2HNO_3 \longrightarrow H_2SO_4 + 2NO_2$$

(2) Hydrogen sulphide is oxidised to sulphur.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

$$H_2S + O \longrightarrow H_2O + S$$

$$H_2S + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + S$$

(3) Ferrous sulphate is oxidised to ferric sulphate in presence of H<sub>2</sub>SO<sub>4</sub>.

$$2HNO_{3} \longrightarrow H_{2}O + 2NO + 3O$$

$$[2FeSO_{4} + H_{2}SO_{4} + O \longrightarrow Fe_{2}(SO_{4})_{3} + H_{2}O] \times 3$$

 $6FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$ 

NO is absorbed by ferrous sulphate and a dark brown ring of nitroso ferrous sulphate is formed. This is the ring test for nitrates. [Nitrate + ferrous sulphate + conc. sulphuric acid  $\longrightarrow$  a brown ring (FeSO<sub>4</sub>NO)]

(4) Iodine is liberated from KI.

$$2HNO_3 \longrightarrow 2NO + H_2O + 3O$$

$$[2KI + 2HNO_3 + O \longrightarrow 2KNO_3 + I_2 + H_2O] \times 3$$

$$6KI + 8HNO_3 \longrightarrow 6KNO_3 + 2NO + 3I_2 + 4H_2O$$

(5) HBr, HI are oxidised to Br<sub>2</sub> and I<sub>2</sub>, respectively.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

$$2HBr + O \longrightarrow H_2O + Br_2$$

$$2HBr + 2HNO_3 \longrightarrow Br_2 + 2NO_2 + 2H_2O$$
Similarly,  $2HI + 2HNO_3 \longrightarrow I_2 + 2NO_2 + 2H_2O$ 

(6) Ferrous sulphide is oxidised to ferrous sulphate.

$$[2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 4$$

$$FeS + 4O \longrightarrow FeSO_4$$

$$FeS + 8HNO_3 \longrightarrow FeSO_4 + 8NO_2 + 4H_2O$$

(7) Stannous chloride is oxidised to stannic chloride in presence of HCl.

$$[SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2H] \times 7$$

$$2HNO_3 + 14H \longrightarrow NH_2OH + NH_3 + 5H_2O$$

$$Hydroxylamine$$

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$7SnCl_2 + 14HCl + 3HNO_3 \longrightarrow 7SnCl_4 + NH_2OH + NH_4NO_3 + 5H_2O$$

(8) Cane sugar is oxidised to oxalic acid.

$$C_{12}H_{22}O_{11} + 36HNO_3 \longrightarrow 6(COOH)_2 + 36NO_2 + 23H_2O$$

#### (C) Action on metals

Most of the metals with the exception of noble metals like gold and platinum are attacked by nitric acid. Nitric acid plays a double role in the action of metals, *i.e.*, it acts as an acid as well as an oxidising agent. Armstrong postulated that primary action of nitric acid is to produce hydrogen in the nascent form. Before this hydrogen is allowed to escape, it reduces the nitric acid into number of products like NO<sub>2</sub>, NO, N<sub>2</sub>O, N<sub>2</sub> or NH<sub>3</sub> according to the following reactions:

Metal + HNO<sub>3</sub> 
$$\longrightarrow$$
 Nitrate + H  
2HNO<sub>3</sub> + 2H  $\longrightarrow$  2NO<sub>2</sub> + 2H<sub>2</sub>O  
2HNO<sub>3</sub> + 6H  $\longrightarrow$  2NO + 4H<sub>2</sub>O  
2HNO<sub>3</sub> + 10H  $\longrightarrow$  N<sub>2</sub> + 6H<sub>2</sub>O  
2HNO<sub>3</sub> + 16H  $\longrightarrow$  2NH<sub>3</sub> + 6H<sub>2</sub>O

The progress of the reaction is controlled by a number of factors:

- (a) the nature of the metal,
- (b) the concentration of the acid,
- (c) the temperature of the reaction,
- (d) the presence of other impurities.

According to another view, reduction of nitric acid with nascent hydrogen occurs only in the case of those metals which are above hydrogen in the electrochemical series. In the case of metals which are below the hydrogen in the electrochemical series, the formation of hydrogen is not possible and thus metals are oxidised by nitric acid. The oxide formed being basic in nature reacts with nitric acid to form nitrate.

$$HNO_3 \longrightarrow O$$
 $Metal + O \longrightarrow Oxide$ 
 $Oxide + HNO_3 \longrightarrow Nitrate + Water$ 

### (1) Metals which are above hydrogen in electrochemical series :

(i) When hydrogen is given off: Magnesium and manganese are the metals that liberate hydrogen with dilute nitric acid.

$$\begin{array}{c} \text{Mg} + 2\text{HNO}_3 \longrightarrow \text{Mg(NO}_3)_2 + \text{H}_2 \\ \\ \text{Dilute} \end{array}$$

$$\text{Mn} + 2\text{HNO}_3 \longrightarrow \text{Mn(NO}_3)_2 + \text{H}_2 \\ \\ \text{Dilute} \end{array}$$

# (ii) When metal nitrates are formed and nitric acid is reduced:

(a) Zinc: It reacts with very dilute nitric acid (6%) to form ammonium nitrate.

$$[Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4$$

$$HNO_3 + 8H \longrightarrow NH_3 + 3H_2O$$

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$
V. dilute

It reacts with dil. HNO $_3\,(20\%)$  to form nitrous oxide (N $_2\mathrm{O}$ ).

$$[Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4$$

$$2HNO_3 + 8H \longrightarrow N_2O + 5H_2O$$

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

It reacts with conc. HNO<sub>3</sub> (70%) to form nitrogen dioxide (NO<sub>2</sub>).

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H$$

$$[HNO_3 + H \longrightarrow NO_2 + H_2O] \times 2$$

$$Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

$$Conc.$$

**(b) Iron:** Iron with very dilute nitric acid forms ammonium nitrate.

$$4Fe + 10HNO_3 \longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$
Ferrous nitrate

Iron with dilute nitric acid forms nitrous oxide.

$$4Fe + 10HNO_3 \longrightarrow 4Fe(NO_3)_2 + N_2O + 5H_2O$$
Dilute

Iron with conc. HNO<sub>3</sub> forms nitrogen dioxide (NO<sub>2</sub>).

Fe + 3HNO<sub>3</sub> 
$$\longrightarrow$$
 Fe(NO<sub>3</sub>)<sub>3</sub> + 3H  
[HNO<sub>3</sub>+H  $\longrightarrow$  NO<sub>2</sub> + H<sub>2</sub>O] × 3  
Fe + 6HNO<sub>3</sub>  $\longrightarrow$  Fe(NO<sub>3</sub>)<sub>3</sub> + 3NO<sub>2</sub> + 3H<sub>2</sub>O  
Conc. Ferric nitrate

Iron is rendered passive by highly concentrated nitric acid 80%.

(c) Tin: Tin forms ammonium nitrate with dilute nitric acid.

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$
Dilute Stannous nitrate

Tin forms metastannic acid with conc. HNO<sub>3</sub> and evolves nitrogen dioxide.

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$
  
Hot conc. Metastannic acid

(d) Lead: It forms nitric oxide with dilute HNO<sub>3</sub>.

[Pb + 2HNO<sub>3</sub>  $\longrightarrow$  Pb(NO<sub>3</sub>)<sub>2</sub> + 2H] × 3

[HNO<sub>3</sub> + 3H  $\longrightarrow$  NO + 2H<sub>2</sub>O] × 2

3Pb + 8HNO<sub>3</sub>  $\longrightarrow$  3Pb(NO<sub>3</sub>)<sub>2</sub> + 2NO + 4H<sub>2</sub>O

It forms nitrogen dioxide with conc. HNO<sub>3</sub>.

Pb + 2HNO<sub>3</sub> 
$$\longrightarrow$$
 Pb(NO<sub>3</sub>)<sub>2</sub> + 2H  
[HNO<sub>3</sub> + H  $\longrightarrow$  NO<sub>2</sub> + H<sub>2</sub>O] × 2  
Pb + 4HNO<sub>3</sub>  $\longrightarrow$  Pb(NO<sub>3</sub>)<sub>2</sub> + 2NO<sub>2</sub> + 2H<sub>2</sub>O

# (2) Metals which are below hydrogen in the electrochemical series:

(a) Copper: Copper with cold dil. HNO<sub>3</sub> forms nitric oxide (NO).

$$2HNO_{3} \longrightarrow H_{2}O + 2NO + 3O$$

$$[Cu + O \longrightarrow CuO] \times 3$$

$$[CuO + 2HNO_{3} \longrightarrow Cu(NO_{3})_{2} + H_{2}O] \times 3$$

$$3Cu + 8HNO_{3} \longrightarrow 3Cu(NO_{3})_{2} + 2NO + 4H_{2}O$$

Copper with hot conc. HNO<sub>3</sub> forms nitrogen dioxide (NO<sub>2</sub>).

$$2HNO_{3} \longrightarrow H_{2}O + 2NO_{2} + O$$

$$Cu + O \longrightarrow CuO$$

$$CuO + 2HNO_{3} \longrightarrow Cu(NO_{3})_{2} + H_{2}O$$

$$Cu + 4HNO_{3} \longrightarrow Cu(NO_{3})_{2} + 2NO_{2} + 2H_{2}O$$

$$Hot conc.$$

**(b)** Silver: Silver behaves similarly as copper.

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO + 2H_2O$$

$$Dilute$$

$$Ag + 2HNO_3 \longrightarrow AgNO_3 + NO_2 + H_2O$$

(c) Mercury: Mercury with dilute nitric acid forms mercurous nitrate and nitric oxide.

$$2HNO_{3} \longrightarrow H_{2}O + 2NO + 3O$$

$$[2Hg + O \longrightarrow Hg_{2}O] \times 3$$

$$[Hg_{2}O + 2HNO_{3} \longrightarrow Hg_{2}(NO_{3})_{2} + H_{2}O] \times 3$$

$$6Hg + 8HNO_{3} \longrightarrow 3Hg_{2}(NO_{3})_{2} + 2NO + 4H_{2}O$$
Dilute

Mercurous nitrate

Mercury with conc. HNO<sub>3</sub> forms mercuric nitrate and nitrogen dioxide.

$$2HNO_{3} \longrightarrow H_{2}O + 2NO_{2} + O$$

$$Hg + O \longrightarrow HgO$$

$$HgO + 2HNO_{3} \longrightarrow Hg(NO_{3})_{2} + H_{2}O$$

$$Hg + 4HNO_{3} \longrightarrow Hg(NO_{3})_{2} + 2NO_{2} + 2H_{2}O$$

$$Conc. \qquad Mercuric nitrate$$

#### Summary:

Concentration of nitric acid	Metal	Main products
Very Dilute HNO <sub>3</sub>	Mg, Mn	H <sub>2</sub> + metal nitrate
very Dilute 111403	Fe, Zn, Sn	NH <sub>4</sub> NO <sub>3</sub> + metal nitrate
	Pb, Cu, Ag, Hg	NO + metal nitrate
Dilute HNO <sub>3</sub>	Fe, Zn	N <sub>2</sub> O + metal nitrate
	Sn	$NH_4NO_3 + Sn(NO_3)_2$
	Zn, Fe, Pb, Cu, Ag	NO <sub>2</sub> + metal nitrate
Conc. HNO <sub>3</sub>	Sn	NO <sub>2</sub> + H <sub>2</sub> SnO <sub>3</sub> Metastannic acid

(3) Metals which become passive: The concentrated nitric acid renders metals like iron, cobalt, nickel, chromium, etc., passive. Aluminium is also rendered passive by nitric acid.

The inertness exhibited by metals under conditions in which chemical activity is expected is known as passivity. For example, iron displaces copper from copper sulphate solution. This property of iron is lost if it is dipped in conc. HNO<sub>3</sub>. The phenomenon of passivity (inertness) is best explained by assuming the formation of a thin film of oxide on the surface of the metal which prevents the action of the reagent.

(4) Metals which do not react: Noble metals like gold, platinum, iridium, rhodium, etc., are not acted upon by nitric acid. However, these metals dissolve in aqua-regia (3 parts conc. HCl and one part conc. HNO<sub>3</sub>). Aqua-regia forms nascent chlorine which attacks these metals.

#### Gold:

$$[HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2Cl] \times 3$$

$$[Au + 3Cl \longrightarrow AuCl_3] \times 2$$

$$[AuCl_3 + HCl \longrightarrow HAuCl_4] \times 2$$

$$2Au + 3HNO_3 + 11HCl \longrightarrow 2HAuCl_4 + 3NOCl + 6H_2O$$
Chloroauric acid

#### Platinum:

$$[HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2Cl] \times 2$$

$$Pt + 4Cl \longrightarrow PtCl_4$$

$$PtCl_4 + 2HCl \longrightarrow H_2PtCl_6$$

$$Pt + 2HNO_3 + 8HCl \longrightarrow H_2PtCl_6 + 2NOCl + 4H_2O$$

$$Chloroplatinic acid$$

### (D) Action on organic compounds

(i) Nitration: The replacement of one or more hydrogen atoms of an organic compound by a nitro group (— $NO_2$ ) is known as nitration. The nitration occurs in presence of conc. sulphuric acid with the formation of nitronium ion,  $NO_2^+$ .

$$HNO_3 + 2H_2SO_4 \Longrightarrow NO_2^+ + 2HSO_4^- + H_3O_4^+$$
  
Nitronium ion Hydronium io

Benzene and phenol when treated with a mixture of conc. HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub> form nitrobenzene and trinitro phenol (picric acid) respectively.

Benzene + HONO<sub>2</sub> 
$$\xrightarrow{H_2SO_4}$$
  $\xrightarrow{NO_2}$   $\xrightarrow{H_2O}$  Nitrobenzene OH  $\xrightarrow{OH}$   $\xrightarrow{OH}$   $\xrightarrow{NO_2}$  + 3HONO<sub>2</sub>  $\xrightarrow{H_2SO_4}$   $\xrightarrow{O_2N}$   $\xrightarrow{NO_2}$  + 3H<sub>2</sub>O Phenol NO<sub>2</sub> Picric acid

Glycerol with conc. HNO<sub>3</sub> in presence of conc. H<sub>2</sub>SO<sub>4</sub> below 25°C forms glycerol trinitrate (Nitroglycerine).

$$\begin{array}{c|c} \text{CH}_2\text{OH} & \text{CH}_2\text{ONO}_2 \\ | & \text{CHOH} + 3\text{HONO}_2 & \xrightarrow{\text{H}_2\text{SO}_4} & \text{CHONO}_2 + 3\text{H}_2\text{O} \\ | & \text{CH}_2\text{OH} & \text{CH}_2\text{ONO}_2 \\ | & \text{Nitroglycerine} \end{array}$$

**Action on proteins:** Nitric acid attacks proteins forming a yellow nitro compound called **xanthoprotein**. It, therefore, stains skin and renders wool yellow. This property is utilised for the test of proteins.

(ii) Oxidation: A number of organic compounds are oxidised.

Sawdust catches fire when nitric acid is poured on it. Turpentine oil bursts into flames when treated with fuming nitric acid. Cane sugar is oxidised to oxalic acid. Toluene is oxidised to benzoic acid with dil. HNO<sub>3</sub>.

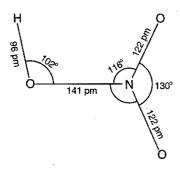
$$\begin{array}{cccc}
CH_3 & COOH \\
& & + & 3O \xrightarrow{\text{Dil. HNO}_3} & & & + & H_2O
\end{array}$$
Benzoic acid

Uses: Nitric acid is used:

- (i) in the manufacture of explosives like T.N.T. (trinitrotoluene), picric acid, nitroglycerine, dynamite, etc.
- (ii) in the manufacture of fertilizers like ammonium nitrate, basic calcium nitrate, etc.
- (iii) in the manufacture of artificial silk, dyes, drugs, perfumes, etc.
  - (iv) in the purification of silver and gold.
  - (v) as a laboratory reagent.
- (vi) as a solvent for metals, for etching designs on wares of brass, bronze, etc.
  - (vii) in the preparation of aqua-regia.
  - (viii) in the manufacture of sulphuric acid.
  - (ix) for nitration of organic compounds.
- (x) for the manufacture of nitrates such as silver nitrate, sodium nitrate, potassium nitrate, etc.

**Structure:** Nitric acid is a monobasic acid, *i.e.*, the molecule consists of one hydroxyl group as it is formed by the hydrolysis of nitryl chloride, NO<sub>2</sub>Cl. It may be structurally represented as below:

Gaseous nitric acid is a planar molecule. The bond lengths and bond angles as present in the molecule are represented in the figure:



It is supposed to exist in two resonating forms.

## 10.5 NITRATES

The salts of nitric acid are called nitrates. Sodium and potassium nitrates occur in nature while others are prepared by the action of nitric acid on metals, metallic oxides, hydroxides, carbonates, bicarbonates, sulphites, etc.

$$\begin{array}{c} \text{Ag} + 2\text{HNO}_3 \longrightarrow \text{AgNO}_3 + \text{NO}_2 + \text{H}_2\text{O} \\ \text{KOH} + \text{HNO}_3 \longrightarrow \text{KNO}_3 + \text{H}_2\text{O} \\ \text{CaCO}_3 + 2\text{HNO}_3 \longrightarrow \text{Ca(NO}_3)_2 + \text{H}_2\text{O} + \text{CO}_2 \end{array}$$

$$NaHCO_3 + HNO_3 \longrightarrow NaNO_3 + H_2O + CO_2$$
  
 $Na_2SO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + SO_2 + H_2O$ 

**Properties: (i)** Nitrates are generally soluble in water. A few nitrates hydrolyse.

$$Bi(NO_3)_3 + 3H_2O \Longrightarrow Bi(OH)_3 + 3HNO_3$$
  
White ppt.

- (ii) Action of heat: Nitrates are decomposed on heating.
  - (a) Alkali nitrates form nitrites and oxygen on heating.

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$
  
 $2KNO_3 \longrightarrow 2KNO_2 + O_2$ 

(b) Nitrates of alkaline earth metals and heavy metals decompose to give mixture of nitrogen dioxide and oxygen along with a solid residue of metal oxide.

$$2\text{Ca}(\text{NO}_3)_2 \longrightarrow 2\text{CaO} + 4\text{NO}_2 + \text{O}_2$$
  
 $2\text{Pb}(\text{NO}_3)_2 \longrightarrow 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$   
 $2\text{Cu}(\text{NO}_3)_2 \longrightarrow 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$ 

(c) Nitrates of metals of low chemical activity decompose into corresponding metals and mixture of nitrogen dioxide and oxygen.

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$
  
 $Hg(NO_3)_2 \longrightarrow Hg + 2NO_2 + O_2$ 

(d) Ammonium nitrate decomposes to form nitrous oxide.

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

(iii) Action of conc. H<sub>2</sub>SO<sub>4</sub>: When heated with conc. H<sub>2</sub>SO<sub>4</sub>, nitrates undergo double decomposition reaction forming free nitric acid. Some of the nitric acid get decomposed to give brown fumes of nitrogen dioxide.

$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$
  
 $4HNO_3 \longrightarrow 4NO_2 + 2H_2O + O_2$ 

(iv) Nitrates are good oxidising agents. These are used in gun powder and explosives.

#### **Tests for Nitrates**

- (a) Nitrate + conc.  $H_2SO_4 \xrightarrow{Heat}$  Brown fumes of  $NO_2$  are given off.
- (b) Nitrate + conc.  $H_2SO_4$  + copper turnings  $\xrightarrow{\text{Heat}}$  quick evolution of brown fumes of  $NO_2$ .
- (c) Aq. soln. of nitrate + freshly prepared soln. of ferrous sulphate + conc.  $H_2SO_4$  which is added carefully by the side of the test tube  $\longrightarrow$  A brown ring is formed at the junction of two liquids.

  - (e) Nitrate + Zn metal + dil.  $H_2SO_4 \xrightarrow{Boil \text{ for } 5 \text{ minutes}} Solution$

The solution is treated with few drops each of KI and starch solutions. Violet colouration is obtained.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$

Nascent hydrogen reduces nitrate into nitrite.

$$NaNO_3 + 2H \longrightarrow NaNO_2 + H_2O$$
  
 $2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$ 

HNO<sub>2</sub> acid evolves iodine from KI which gives violet colouration with starch.

#### **DISTINCTION BETWEEN NITRITES AND NITRATES**

	Test	Nitrites	Nitrates
1.	Treat the salt with dilute HCl.	Brown fumes which turn FeSO <sub>4</sub> solution black.	No action.
2.		Dark brown colour even with dilute $H_2SO_4$ .	
3.	solution of the salt	lodine evolved, give blue colour with starch.	No action
4.	To the acidified salt solution add KMnO <sub>4</sub> solution.		No action.
5.	To the solution add brucine solution.	No action.	Red colouration.



## **PHOSPHORUS**

Phosphorus was discovered by Brand in 1669. Scheele isolated it from bone ash and Lavoisier in 1777 proved that phosphorus is an element. It glows in the dark and was, therefore, called phosphorus (Greek word, *phos* = light, and *phero* = I carry).

**Occurrence:** Since phosphorus is an active element, it is not found free in nature. It is widely distributed in nature in the combined state. It occurs as phosphates in the rocks and in the soil and as phosphoproteins in all living beings. Deoxyribonucleic acid (DNA) is a chainlike biological molecule in which informations about inheritable traits resides, contains phosphate groups along the length of its chain. Similarly, ATP (adenosine triphosphate), the energy containing molecule of living organisms, contains phosphate groups. It is an essential constituent of bones, teeth, blood and nervous tissues. It is necessary for the growth of plants. Bone ash contains about 80% calcium phosphate. It is present in milk, eggs and guano (excreta of seabirds). The principal minerals of phosphorus are:

(i) Phosphorite or phosphate rock Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>

(ii) Fluorapatite, 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·CaF<sub>2</sub> or Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F

(iii) Chlorapatite, 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·CaCl<sub>2</sub> or Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl

**Extraction:** Phosphorus is extracted either from phosphorite or bone ash by the application of following two processes:

- (i) Retort process or old process.
- (ii) Electrothermal process or modern process.

## (i) Retort process or old process:

The phosphorite mineral or bone ash is digested with concentrated sulphuric acid (about 60%). Insoluble calcium sulphate and orthophosphoric acid are formed.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$

The syrupy liquid is separated from insoluble residue by filtration. The liquid is evaporated when it changes into metaphosphoric acid with evolution of water.

$$H_3PO_4 \longrightarrow HPO_3 + H_2O$$
Metaphosphoric

The metaphosphoric acid is mixed with powdered coke and distilled in fireclay retorts at a bright red heat (Fig. 10.8). The acid is reduced to phosphorus by carbon which comes in vapourised form. The vapours are condensed below water.

$$4HPO_3 + 10C \longrightarrow P_4 + 10CO + 2H_2O$$

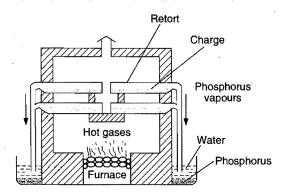


Fig. 10.8 Retort process

# (ii) Electrothermal process or modern process:

Phosphorus is prepared now a days by the direct reduction of mineral phosphorite, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> by carbon in presence of silica. The mixture of phosphorite, (phosphate rock) with coke (C) and quartz sand (SiO<sub>2</sub>) is dried and then introduced into the electric furnace (Fig. 10.9). The furnace is an iron tank

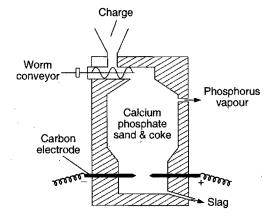


Fig. 10.9

lined inside with refractory bricks. Carbon electrodes are fitted on either side of the furnace. The furnace has two exits, one for removal of vapours in the upper part of the furnace and other for removal of slag in the lower part of the furnace. The charge is introduced through the closed hopper arrangement.

The mixture is heated at 1400-1500°C by the discharge of an alternating current between carbon electrodes. Silica combines with calcium phosphate and forms phosphorus pentoxide which is reduced by carbon into phosphorus. The overall reaction is,

$$[Ca3(PO4)2 + 3SiO2 \longrightarrow 3CaSiO3 + P2O5] \times 2$$
  
$$2P2O5 + 10C \longrightarrow P4 + 10CO$$

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow 6CaSiO_3 + 10CO + P_4$$

Vapours of phosphorus and carbon monoxide leave the furnace through the upper exit and are condensed under water. The other product, calcium silicate glass (called *slag*) is tapped out periodically by an exit from the bottom of the furnace.

**Purification:** Phosphorus obtained is further purified by melting under acidified potassium dichromate solution when the impurities are oxidised. It is redistilled.

## Allotropic modifications of phosphorus

Phosphorus exists in a number of allotropic forms. These forms are:

- (i) Yellow or white phosphorus (ii) Red phosphorus
- (iii) Scarlet phosphorus
- (iv) α-black phosphorus
- (v) β-black phosphorus
- (vi) Violet phosphorus

The main allotropic forms, however, are white phosphorus and red phosphorus.

## White or yellow phosphorus:

This is the common variety and is obtained by the methods described above. This form is chemically very active.

**Properties:** (i) White phosphorus is a molecular, transparent waxy solid, (sp. gr. 1.8) with the formula P<sub>4</sub>.

- (ii) The pure form is white but attains yellow colour on long standing due to the formation of a thin film of the red variety on the surface.
  - (iii) It is a soft metal and can be cut easily with knife.
- (iv) It has characteristic garlic smell and is poisonous in nature. 0.15 g is the fatal dose. Vapours are also injurious. Persons working with phosphorus develop a disease in which the jaw bones decay. This disease is known as **phossy jaw.**
- (v) It is insoluble in water but readily soluble in carbon disulphide.
  - (vi) It melts at 44°C into a yellow liquid. It boils at 280°C.
- (vii) In contact with air, it undergoes slow combustion and glows in dark. This property is called **phosphorescence**.
- (viii) Its ignition temperature is low (about 30°C). It readily catches fire giving dense fumes of phosphorus pentoxide. It is, therefore, kept in water.

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$
 or  $2P_2O_5$ 

(ix) It dissolves in caustic alkalies on boiling in an inert atmosphere and forms phosphine.

$$\begin{array}{c} P_4 \,+\, 3NaOH \,+\, 3H_2O \longrightarrow 3NaH_2PO_2 \\ \text{Caustic} \\ \text{soda} \end{array} \begin{array}{c} + \quad PH_3 \\ \text{Phosphine} \end{array}$$

- (x) It is very poisonous and very reactive. If white phosphorus is left exposed to air, it bursts spontaneously into flame. Because of its reactivity with oxygen, white phosphorus is stored under water, in which it is insoluble.
- (xi) It directly combines with halogens forming first, trihalides and then pentahalides.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$
;  $P_4 + 10\hat{Cl}_2 \longrightarrow 4PCl_5$ 

(xii) It combines with a number of metals forming phosphides.

$$6Mg + P_4 \longrightarrow 2Mg_3P_2$$
 (Magnesium phosphide)  
 $6Ca + P_4 \longrightarrow 2Ca_3P_2$  (Calcium phosphide)

- (xiii) It combines with sulphur with explosive violence forming a number of sulphides such as  $P_2S_3$ ,  $P_2S_5$ ,  $P_4S_3$  and  $P_4S_7$ .
- (xiv) It acts as a strong reducing agent. It reduces nitric acid and sulphuric acid.

$$[2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 10$$

$$P_4 + 10 O + 6H_2O \longrightarrow 4H_3PO_4$$

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

$$[H_2SO_4 \longrightarrow H_2O + SO_2 + O] \times 10$$

$$P_4 + 10 O + 6H_2O \longrightarrow 4H_3PO_4$$

$$P_4 + 10H_2SO_4 \longrightarrow 4H_3PO_4 + 10SO_2 + 4H_2O$$

It reduces solutions of copper, silver and gold salts to corresponding metals.

 $P_4 + 10CuSO_4 + 16H_2O \longrightarrow 10Cu + 4H_3PO_4 + 10H_2SO_4$ When the solution is heated, cuprous phosphide is formed.

$$3P_4 + 12CuSO_4 + 24H_2O \xrightarrow{\text{Heat}} 4Cu_3P + 8H_3PO_3 + 12H_2SO_4$$
  
 $P_4 + 20AgNO_3 + 16H_2O \longrightarrow 20Ag + 4H_3PO_4 + 20HNO_3$ 

(xv) When heated in inert atmosphere at 240°C, it changes into red variety.

Yellow P 
$$\xrightarrow{240-250^{\circ}\text{C}}$$
 Red P

**Structure:** The vapour density of white phosphorus between 500-700°C, is 62 which corresponds to the molecular formula P<sub>4</sub>. The four phosphorus atoms lie at the corners of a regular tetrahedron. Each phosphorus atom is linked to each of the other three atoms by covalent bonds. The P—P bond length is equal to 2.21 Å. The bond angle is equal to 60° which suggests that the molecule is under strain and hence active in nature.

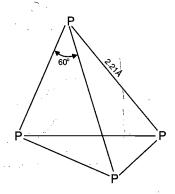


Fig. 10.10

## Red phosphorus

**Preparation:** Red phosphorus is obtained by heating yellow phosphorus, between 240-250°C, in presence of an inert gas for several hours. The heating is done in an egg shaped iron vessel provided with a upright tube closed by safety valve. The thermometers placed in iron tubes help to regulate the temperature.

Yellow phosphorus is taken in egg shaped vessel and air inside is replaced by coal gas or carbon dioxide. A trace of iodine is added which helps in the transformation. The vessel is carefully heated to 250°C. The temperature is not allowed to rise above 250°C otherwise the reaction goes out of control. In case the pressure inside the vessel becomes too high the safety valve is lifted to allow the escape of some vapours. The heating is done for several days. Red phosphorus obtained is powdered. It possesses yellow phosphorus as impurity. This is removed by boiling with caustic soda solution. Red phosphorus is not affected by caustic soda and remains undissolved. This is thoroughly washed with water and finally dried. Red phosphorus is much less reactive than white phosphorus and can be stored in the presence of air.

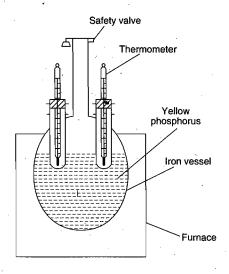


Fig. 10.11

**Properties:** (a) It is dark red powder with specific gravity 2.1.

- (b) It is odourless and non-poisonous in nature.
- (c) It is insoluble in water as well as in carbon disulphide.
- (d) It does not show phosphorescence.
- (e) It sublimes in absence of air at 290°C.
- (f) Its ignition temperature is high, i.e., 260°C.
- (g) Chemically, it is not active in nature. It burns when heated above 260°C to form phosphorus pentoxide.
  - (h) It does not react with caustic alkalies.
- (i) It combines with halogens, sulphur and metals when heated.

$$\begin{array}{c} 2P + 5Cl_2 \xrightarrow{\quad Heat \quad} 2PCl_5 \\ 2P + 3S \xrightarrow{\quad Heat \quad} P_2S_3 \\ P + 3Na \xrightarrow{\quad Heat \quad} Na_3P \end{array}$$

(j) It changes to white phosphorus when it is vaporised and the vapours are condensed.

**Structure of red phosphorus:** The exact structure of red phosphorus is not yet known. It is regarded as a polymer consisting of chains of P<sub>4</sub> tetrahedral linked together possibly in the manner as shown in Fig. 10.12.

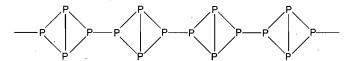


Fig. 10.12 Proposed molecular structure of red phosphorus

#### COMPARISON BETWEEN WHITE AND RED PHOSPHORUS

Property	White phosphorus	Red phosphorus
1. Physical state	Soft waxy solid.	Brittle powder.
2. Colour	White when pure.	Red.
	Attains yellow colour on standing.	
3. Odour	Garlic	Odourless.
4. Specific gravity	1.8	2.1
5. Melting point	44°C	Sublimes in absence of air at 290°C.
6. Ignition temperat	ture Low, 30°C	High, 260°C.
7. Solubility in wat	er Insoluble.	Insoluble.
8. Solubility in CS2	Soluble.	Insoluble.
9. Physiological act	ion Poisonous.	Non-poisonous.
10. Chemical activity	y Very active.	Less active.
11. Stability	Unstable.	Stable.
12. Phosphorescence	Glows in dark.	Does not glow in dark.
13. Burning in air	Forms P <sub>4</sub> O <sub>10</sub> .	Forms P <sub>4</sub> O <sub>10</sub> .
14. Reaction with Na	OH Evolves phosphine.	No action.
15. Action of Cl <sub>2</sub>	Combines spontaneously to form PCl <sub>3</sub> and PCl <sub>5</sub> .	
16. Reaction with HNO <sub>3</sub>	hot Forms H <sub>3</sub> PO <sub>4</sub> .	Forms H <sub>3</sub> PO <sub>4</sub> .
17. Molecular formu	la P₄	Complex polymer.

**Uses of phosphorus:** (i) Red phosphorus is largely used in the match industry. It is relatively nontoxic and is used in the striking surface of safety matches. Red phosphorus or scarlet phosphorus is preferred to yellow variety.

- (ii) Yellow phosphorus is used as a rat poison.
- (iii) Red phosphorus is used for the preparation of HBr and HI.
- (iv) Radioactive phosphorus (P<sup>32</sup>) is used in the treatment of leukemia and other blood disorders.
- (v) It is used for making incendiary bombs and smoke screens.
- (vi) It is used in the manufacture of phosphor bronze, an alloy of phosphorus, copper and tin.
- (vii) It is used in the manufacture of compounds like hypophosphites (medicine), phosphorus chlorides employed in industry, calcium phosphide used in making Holme's signals and orthophosphoric acid.

## 10.7 COMPOUNDS OF PHOSPHORUS

## 1. Phosphine, PH<sub>3</sub>

It is analogous to ammonia. It was discovered by Gengembre in 1783. It is also known as **hydrogen phosphide** or **phosphoretted hydrogen.** 

**Laboratory preparation:** It is prepared by boiling yellow phosphorus with a concentrated solution of sodium hydroxide in an inert atmosphere.

$$\begin{array}{c} P_4 \,+\, 3NaOH \,+\, 3H_2O \longrightarrow & 3NaH_2PO_2 \quad + \ PH_3 \\ \text{Sodium hypophosphite} \end{array}$$

Besides  $PH_3$ , small amounts of hydrogen  $(H_2)$  and phosphorus dihydride  $(P_2H_4)$  are also formed.

$$P_4 + 4NaOH + 4H_2O \longrightarrow 4NaH_2PO_2 + 2H_2$$
  
 $3P_4 + 8NaOH + 8H_2O \longrightarrow 8NaH_2PO_2 + 2P_2H_4$ 

A concentrated solution of sodium hydroxide is taken in a round bottom flask. Few pieces of yellow phosphorus are

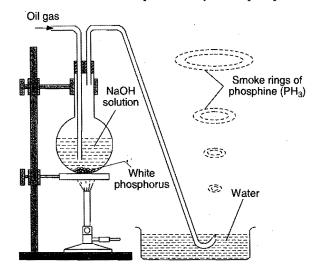


Fig. 10.13

dropped into it. Coal gas, oil gas or carbon dioxide is then bubbled through the flask to displace the air from the apparatus. The flask is then heated.  $PH_3$  is evolved. It is driven out along with a current of inert gas. As soon as the bubbles of the gas come in contact with air, they catch fire spontaneously forming rings of smoke known as vortex rings. This combustion is due to the presence of highly inflammable phosphorus dihydride  $(P_2H_4)$ .

2P<sub>2</sub>H<sub>4</sub> + 7O<sub>2</sub> 
$$\longrightarrow$$
 4HPO<sub>3</sub> + 2H<sub>2</sub>O Metaphosphoric

P<sub>2</sub>H<sub>4</sub> can be removed from phosphine by the following methods:

- (i) By passing the evolved gas through a freezing mixture which condenses P<sub>2</sub>H<sub>4</sub>.
- (ii) By passing the gas through HI. PH<sub>3</sub> is absorbed forming phosphonium iodide. This on treatment with caustic potash gives pure phosphine.

$$PH_4I + KOH \longrightarrow KI + H_2O + PH_3$$

**Note:** Pure phosphine can be obtained by using alcoholic potassium hydroxide in place of aqueous NaOH solution. Phosphine can also be prepared by the application of following reactions:

(i) By heating phosphorus acid.

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

(ii) By treating phosphonium iodide with 30% KOH solution.

$$PH_4I + KOH \longrightarrow KI + H_2O + PH_3$$

The evolved gas is first passed through HCl (decomposes P<sub>2</sub>H<sub>4</sub>) and then through NaOH (HI absorbed). This gives pure PH<sub>3</sub>.

(iii) By treating aluminium phosphide with dilute H<sub>2</sub>SO<sub>4</sub>.

$$2AIP + 3H_2SO_4 \longrightarrow AI_2(SO_4)_3 + 2PH_3$$

(iv) By doing hydrolysis of calcium phosphide with water or dil. HCl.

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

## Physical properties:

- (a) It is a colourless gas having unpleasant garlic-like odour or rotten fish odour.
  - (b) It is heavier than air and sparingly soluble in water.
  - (c) It liquefies at -89°C and solidifies at -134°C.
  - (d) It is poisonous in nature.

#### Chemical properties:

(a) **Decomposition:** When heated out of contact of air to 440°C or when electric sparks are passed through, phosphine decomposes into red phosphorus and hydrogen.

$$4PH_3 \longrightarrow P_4 + 6H_2$$

**(b)** Combustibility: A pure sample of phosphine is not spontaneously inflammable. It burns in air or oxygen when heated at 150°C.

$$2PH_3 + 4O_2 \longrightarrow P_2O_5 + 3H_2O$$

The spontaneous inflammability of phosphine at the time of preparation is due to the presence of highly inflammable phosphorus dihydride, P<sub>2</sub>H<sub>4</sub>. This property is used in making

Holme's signal. A mixture of calcium carbide and calcium phosphide is placed in metallic containers. Two holes are made and the container is thrown into the sea. Water enters and produces acetylene and phosphine respectively. The gaseous mixture catches fire spontaneously due to the presence of  $P_2H_4$ . The acetylene produces a bright luminous flame which serves as a signal to the approaching ship.

**(c) Action of chlorine:** Phosphine burns in the atmosphere of chlorine and forms phosphorus pentachloride.

$$PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$$

(d) Basic nature: Phosphine is neutral to litmus. However, it is a weak base, even weaker than ammonia. It reacts with HCl, HBr or HI to form phosphonium compounds.

$$PH_3 + HCl \longrightarrow PH_4Cl$$
 (Phosphonium chloride)  
 $PH_3 + HBr \longrightarrow PH_4Br$  (Phosphonium bromide)  
 $PH_3 + HI \longrightarrow PH_4I$  (Phosphonium iodide)

(e) Action of nitric acid: In contact with nitric acid phosphine begins to burn.

$$[2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 8$$

$$2PH_3 + 8O \longrightarrow P_2O_5 + 3H_2O$$

$$2PH_3 + 16HNO_3 \longrightarrow P_2O_5 + 16NO_2 + 11H_2O$$

(f) Addition compounds: It forms addition compounds with anhydrous  $AlCl_3$  and  $SnCl_4$ .

$$AlCl_3 + 2PH_3 \longrightarrow AlCl_3 \cdot 2PH_3$$
  
 $SnCl_4 + 2PH_3 \longrightarrow SnCl_4 \cdot 2PH_3$ 

When PH<sub>3</sub> is passed through cuprous chloride solution in HCl, it forms an addition compound.

$$Cu_2Cl_2 + 2PH_3 \longrightarrow 2CuCl \cdot PH_3$$

**(g) Formation of phosphides:** (i) When phosphine is passed through copper sulphate solution, a black precipitate of cupric phosphide is formed.

$$3\text{CuSO}_4 + 2\text{PH}_3 \longrightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4$$

(ii) A black precipitate of silver phosphide is formed when phosphine is circulated through silver nitrate solution.

$$3AgNO_3 + PH_3 \longrightarrow Ag_3P + 3HNO_3$$

(iii) When absorbed in mercuric chloride solution, mercuric phosphide is formed.

$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$$

(h) The mixture of  $PH_3$  and  $N_2O$  or  $PH_3$  and NO explodes in presence of electric spark.

$$PH_3 + 4N_2O \longrightarrow H_3PO_4 + 4N_2$$

**Structure of phosphine:** Phosphine is a covalent molecule. It has pyramidal structure like ammonia.



The bond angle H—P—H is 93°.

Uses: (i) For making Holme's signals.

- (ii) For making smoke screens.
- (iii) For making metallic phosphides.

#### **COMPARISON OF PHOSPHINE AND AMMONIA**

Property	Ammonia	Phosphine
1. Physical state	Colourless gas.	Colourless gas.
2. Odour	Characteristic pungent smell.	Unpleasant odour of rotten fish.
3. Molecular formula	NH <sub>3</sub>	PH <sub>3</sub>
4. Solubility	Highly soluble in water.	Sparingly soluble in water.
5. Density	Lighter than air.	Heavier than air.
<ol><li>Physiological action</li></ol>	Non-poisonous.	Poisonous.
7. Stability	Decomposes at 1300°C.	Decomposes at 440°C.
8. Combustibility	It burns in oxygen.	It burns with white bright flame.
	$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$	$2PH_3 + 4O_2 \longrightarrow P_2O_5 + 3H_2O$
<ol><li>Basic character</li></ol>	Basic in nature. Forms ammonium salts with acids.	Weakly basic. Forms phosphonium salts with HCl, HBr and
	$NH_3 + HC1 \longrightarrow NH_4C1$	HI.
		$PH_3 + HCl \longrightarrow PH_4C1$
10. Stability of salts	Fairly stable.	Less stable.
11. Action of chlorine	Forms N <sub>2</sub> , NCl <sub>3</sub> and NH <sub>4</sub> Cl.	Forms PCl <sub>3</sub> and PCl <sub>5</sub> .
12. Action of AgNO <sub>3</sub>	Forms soluble complex, Ag(NH <sub>3</sub> ) <sub>2</sub> NO <sub>3</sub> .	Forms black precipitate Ag <sub>3</sub> P.
<ol> <li>Action of CuSO<sub>4</sub></li> </ol>	Forms soluble complex of blue colour, Cu(NH <sub>3</sub> ) <sub>4</sub> SO <sub>4</sub> .	Forms black precipitate of copper phosphide, Cu <sub>3</sub> P <sub>2</sub> .
<ol><li>Hydrogen bonding</li></ol>	Present.	Absent.
15. Solvent property	Ammonia is a good solvent for many substances.	It does not act as a solvent.
16. Action of hot sodium	Forms sodamide.	Forms phosphide.
	$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2$	$6Na + 2PH_3 \longrightarrow 2Na_3P + 3H_2$
17. Structure	Pyramidal.	Pyramidal.
	Bond angle H—N—H = 107°	Bond angle H—P—H = 93°

## 2. Oxides of Phosphorus

Phosphorus forms three important oxides. These exist in dimeric forms.

- (i) Phosphorus trioxide, P<sub>2</sub>O<sub>3</sub> or P<sub>4</sub>O<sub>6</sub>
- (ii) Phosphorus tetroxide, P<sub>2</sub>O<sub>4</sub> or P<sub>4</sub>O<sub>8</sub>
- (iii) Phosphorus pentoxide, P<sub>2</sub>O<sub>5</sub> or P<sub>4</sub>O<sub>10</sub>

## (i) Phosphorus trioxide, P<sub>4</sub>O<sub>6</sub>

It is formed by burning phosphorus in limited supply of air.

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

The pentoxide, formed in small amount, is removed by passing through glass wool. The vapours of trioxide pass through the glass wool and are condensed in a receiver cooled by a freezing mixture.

Vapours of phosphorus at low pressure react with  $N_2O$  at  $600^{\circ}C$ , to, form  $P_2O_3$ .

$$P_4 + 6N_2O \xrightarrow{600^{\circ}C} 2P_2O_3 + 6N_2$$

Properties: (a) It is a waxy solid having garlic odour.

- (b) It is poisonous in nature.
- (c) It is soluble in benzene or chloroform.
- (d) When heated above 210°C, it forms red phosphorus and another oxide, P<sub>4</sub>O<sub>8</sub>.

$$4P_4O_6 \longrightarrow 3P_4O_8 + 4P$$
Phosphorus
tetroxide

When heated at about 440°C, it dissociates to phosphorus dioxide.

$$2P_2O_3 \longrightarrow 3PO_2 + P$$

(e) In contact with air, it is oxidised to phosphorus pentoxide.

$$P_4O_6 + 2O_2 \longrightarrow P_4O_{10}$$

(f) It burns in chlorine forming oxy-chlorides.

$$\begin{array}{ccccc} P_4O_6 \ + \ 4Cl_2 \longrightarrow & 2POCl_3 \ + & 2PO_2Cl \\ & Phosphorus & Metaphosphorus \\ & oxy-chloride & oxy-chloride \end{array}$$

(g) In cold water, it dissolves slowly forming phosphorus acid.

$$P_4O_6 + 6H_2O(cold) \longrightarrow 4H_3PO_3$$

With hot water, a violent reaction occurs forming orthophosphoric acid and phosphine.

$$P_4O_6 + 6H_2O(hot) \longrightarrow 3H_3PO_4 + PH_3$$

The above reaction is actually the conversion of phosphorus acid into orthophosphoric acid and phosphine.

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

This oxide is known as acid anhydride of phosphorus acid.

Structure of phosphorus trioxide: Its vapour density corresponds to the formula  $P_4O_6$ . In the molecule, the phosphorus atoms lie at tetrahedral positions with respect to each other and the 6 oxygen atoms are inserted in between them (Fig. 10.14). Each phosphorus atom is covalently bonded

to three oxygen atoms and each oxygen atom is bonded to two phosphorus atoms. The bond length P—O is 1.638 Å.

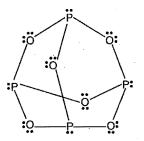


Fig. 10.14

It has 6 P—O—P bonds, 12 sigma bonds and 16 lone pairs of electrons (one lone pair on each P atom and two lone pairs of electrons on each oxygen atom).

## (ii) Phosphorus pentoxide, P<sub>4</sub>O<sub>10</sub>

It is prepared by heating phosphorus in a free supply of air or oxygen.

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

It is further purified by sublimation.

Phosphorus burns in CO2 at 100°C to form P2O5.

$$2P + 5CO_2 \longrightarrow P_2O_5 + 5CO$$

**Properties:** (a) It is a white crystalline compound.

- (b) It is odourless when pure. The usual garlic odour is due to presence of small amount of  $P_4O_6$  as impurity.
  - (c) It is a white solid that sublimes at 360°C.
- (d) It has great affinity for water. The final product is orthophosphoric acid. It is, therefore, termed phosphoric anhydride.

i.e., 
$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

It is, thus, used as a powerful dehydrating or drying agent. It removes water from inorganic and organic compounds like H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, RCOOH, RCONH<sub>2</sub>, etc.

$$2H_2SO_4 + P_4O_{10} \longrightarrow 2SO_3 + 4HPO_3$$

$$4HNO_3 + P_4O_{10} \longrightarrow 2N_2O_5 + 4HPO_3$$

$$4CH_3COOH + P_4O_{10} \longrightarrow 2(CH_3CO)_2O + 4HPO_3$$

$$2CH_3CONH_2 + P_4O_{10} \longrightarrow 2CH_3CN + 4HPO_3$$

It also chars wood, paper, sugar, etc.

(e) When heated strongly with carbon, it forms red phosphorus.

(f) When fused with basic oxides, it forms phosphates.

$$6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$$

(g) 30%  $H_2O_2$  react on  $P_2O_5$  in acetonitrile solution at low temperature to form peroxy monophosphoric acid.

$$P_2O_5 + 2H_2O_2 + H_2O \longrightarrow 2H_3PO_5$$

(h) Mixture of  $P_2O_5$  and  $O_2$  in vapour state combine in presence of electric discharge to form  $P_2O_6$  called phosphorus peroxide.

$$P_2O_5 + \frac{1}{2}O_2 \longrightarrow P_2O_6$$

**Uses:** (i) It is the most effective drying or dehydrating agent below 100°C.

(ii) It is used to manufacture phosphoric acid, an oxoacid. **Structure of phosphorus pentoxide:** Its vapour density corresponds to formula P<sub>4</sub>O<sub>10</sub>. The structure is similar

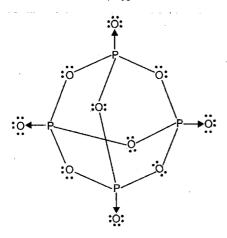


Fig. 10.15

to  $P_4O_6$  (Fig. 10.14) with a difference that each phosphorus atom is linked with an additional oxygen atom with the help of a coordinate linkage involving a lone pair of electrons present on each phosphorus atom (Fig. 10.15).

It has 16 sigma bonds,  $4\pi$  bonds and 24 lone pairs of electrons on oxygen atoms.

## 3. Oxyacids of Phosphorus

Phosphorus forms a number of oxyacids. Common oxyacids are given below:

Name of oxyacid	Formula	Basicity	Oxidation state of P
Hypophosphorus acid	H <sub>3</sub> PO <sub>2</sub>	1.	+1
Phosphorus acid	H <sub>3</sub> PO <sub>3</sub>	2	+3
Orthophosphoric acid	H <sub>3</sub> PO <sub>4</sub>	3	+5
Metaphosphoric acid	HPO <sub>3</sub>	1	+5
Hypophosphoric acid	$H_4P_2O_6$	4	+4
Pyrophosphoric acid	H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	4	+5

All these acids contain phosphorus atom/atoms linked tetrahedrally to four other atoms or groups. Each of them has at least one  $P \rightarrow O$  unit and one  $P \rightarrow OH$  group. The OH group is ionisable but H atom linked directly to P is non-ionisable. Thus, the number of OH groups present decides the basicity of the acid.

## (i) Hypophosphorus acid, H<sub>3</sub>PO<sub>2</sub>

**Preparation:** When yellow phosphorus is boiled with baryta solution, barium hypophosphite is formed which is filtered off.

The barium salt is treated with calculated quantity of sulphuric acid. The insoluble barium sulphate is filtered out and hypophosphorus acid is obtained in the filtrate. The filtrate when evaporated leaves the syrupy mass which can be crystallised by careful cooling below  $0^{\circ}$ C.

$$3Ba(OH)_2 + 8P + 6H_2O \longrightarrow 3Ba(H_2PO_2)_2 + 2PH_3$$

Barium hypophosphite

**Properties:** (a) It is a colourless crystalline solid. It melts at 26.3°C. It is soluble in water.

(b) It is a monobasic acid. It ionises as:

$$H_3PO_2 \rightleftharpoons H^+ + H_2PO_2^-$$
;  $K_a = 10^{-2} \text{ M}$ 

Its salts are known as hypophosphites.

(c) When strongly heated, it evolves phosphine.

$$2H_3PO_2 \longrightarrow H_3PO_4 + PH_3$$

- (d) It acts as a reducing agent.
- (i) It precipitates silver and gold from their solutions.

$$H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$$
  
 $[AgNO_3 + H \longrightarrow Ag + HNO_3] \times 4$ 

$$4AgNO_3 + H_3PO_2 + 2H_2O \longrightarrow 4Ag + H_3PO_4 + 4HNO_3$$

(ii) Mercuric chloride is reduced to mercurous chloride and finally to metallic mercury.

$$\begin{array}{c} H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H \\ 2HgCl_2 + 2H \longrightarrow Hg_2Cl_2 + 2HCl \\ Hg_2Cl_2 + 2H \longrightarrow 2Hg + 2HCl \\ \hline 2HgCl_2 + H_3PO_2 + 2H_2O \longrightarrow 2Hg + H_3PO_4 + 4HCl \end{array}$$

(iii) Copper sulphate is reduced to cuprous hydride.  $4\text{CuSO}_4 + 3\text{H}_2\text{PO}_2 + 6\text{H}_2\text{O} \longrightarrow 2\text{Cu}_2\text{H}_2 + 3\text{H}_3\text{PO}_4 + 4\text{H}_2\text{SO}_4$ 

(iv) Chlorine or iodine is reduced to hydracid.

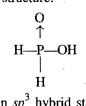
$$H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$$

$$4H + 2Cl_2 \longrightarrow 4HCl$$

$$H_3PO_2 + 2H_2O + 2Cl_2 \longrightarrow H_3PO_4 + 4HCl$$

**Uses:** Some of its salts such as sodium, potassium and calcium hypophosphites are used in medicine as nerve tonics.

**Structure:**  $H_3PO_2$  is a monobasic acid, *i.e.*, it has only one ionisable hydrogen atom or one OH group is present. It is given the following structure:



Phosphorus lies in  $sp^3$  hybrid state.

## (ii) Phosphorus acid, H<sub>3</sub>PO<sub>3</sub>

**Preparation:** (i) It is obtained by dissolving phosphorus trioxide in water.

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

(ii) It is also obtained by hydrolysis of phosphorus trichloride.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

Chlorine is passed over molten white phosphorus under water when phosphorus trichloride formed undergoes hydrolysis.

$$2P + 3Cl_2 \longrightarrow 2PCl_3$$

The solution is heated until the temperature becomes 180°C. On cooling crystals of phosphorus acid are obtained.

**Properties:** (a) It is colourless crystalline compound. It melts at 73°C. It is highly soluble in water.

(b) When heated, it forms orthophosphoric acid and phosphine.

$$4H_3PO_3 \xrightarrow{200^{\circ}C} 3H_3PO_4 + PH_3$$

(c) It is a strong acid. It is dibasic in nature.

$$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^- \rightleftharpoons 2H^+ + HPO_3^-$$
  
 $K_1 = 10^{-1} ; K_2 = 2 \times 10^{-7}$ 

It thus forms two series of salts such as NaH<sub>2</sub>PO<sub>3</sub> and Na<sub>2</sub>HPO<sub>3</sub> known as primary phosphites and secondary phosphites respectively.

(d) It acts as a strong reducing agent. The potential equation is:

$$H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2H$$

It reduces CuSO<sub>4</sub> to Cu, AgNO<sub>3</sub> to Ag, HgCl<sub>2</sub> to Hg<sub>2</sub>Cl<sub>2</sub>, I<sub>2</sub> to HI and acidified KMnO<sub>4</sub> solution.

$$CuSO_4 + 2H \longrightarrow Cu + H_2SO_4$$

$$AgNO_3 + H \longrightarrow Ag + HNO_3$$

$$2HgCl_2 + 2H \longrightarrow Hg_2Cl_2 + 2HCl$$

$$I_2 + 2H \longrightarrow 2HI$$

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$[H_3PO_3 + O \longrightarrow H_3PO_4] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5H_3PO_3 \longrightarrow K_2SO_4 + 2MnSO_4 + 5H_3PO_4 + 3H_2O_4$$

**Structure:** It is dibasic acid, *i.e.*, two hydrogen atoms are ionisable or two hydroxyl groups are present. Thus, the structure is:



The phosphorus lies in  $sp^3$  hybrid state.

## (iii) Orthophosphoric acid, H<sub>3</sub>PO<sub>4</sub>

This acid is commonly called as phosphoric acid.

**Preparation:** (i) It is formed when phosphorus pentoxide is boiled with hot water.

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

(ii) Orthophosphoric acid is also formed when PCl<sub>5</sub> (phosphorus pentachloride) is boiled with water.

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

(iii) Laboratory preparation: The best method for its preparation in the laboratory is to heat red phosphorus with concentrated nitric acid in a flask with a reflux condenser.

$$P + 5HNO_3 \longrightarrow H_3PO_4 + H_2O + 5NO_2$$

The reaction is usually carried out in presence of a crystal of iodine. The iodine acts as a catalyst.

$$P + 3I \longrightarrow PI_{3}$$

$$PI_{3} + 3H_{2}O \longrightarrow H_{3}PO_{3} + 3HI$$

$$3HI + 3HNO_{3} \longrightarrow 3H_{2}O + 3NO_{2} + 3I$$

$$H_{3}PO_{3} + 2HNO_{3} \longrightarrow H_{3}PO_{4} + H_{2}O + 2NO_{2}$$

$$P + 5HNO_{3} \longrightarrow H_{3}PO_{4} + 5NO_{2} + H_{2}O$$

The solution is concentrated till it becomes syrupy at about  $170^{\circ}$ C. It is cooled over conc.  $H_2SO_4$  in vacuum desiccator when crystals of orthophosphoric acid are formed.

**Manufacture:** It is prepared on large scale from bone ash or phosphorite mineral.

(a) By decomposing calcium phosphate present in bone ash or phosphorite mineral with conc. H<sub>2</sub>SO<sub>4</sub>.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$

On standing calcium sulphate settles down and the clear supernatant liquid separates out. The liquid is concentrated when about 85% concentrated orthophosphoric acid is obtained.

(b) The bone ash is dissolved in minimum amount of nitric acid and lead acetate is added as to precipitate lead phosphate. The lead salt is then decomposed by passing  $H_2S$ .

$$Pb_3(PO_4)_2 + 3H_2S \longrightarrow 3PbS + 2H_3PO_4$$
Insoluble Solution

(c) Bone ash or calcium phosphate is converted into phosphorus pentoxide when heated with silica in electric furnace.

 $2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$   $P_4O_{10}$  is then dissolved in hot water.

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

**Properties:** (a) It is a transparent deliquescent crystalline solid. It melts at 42.3°C. It absorbs water and forms colourless syrupy mass. It is highly soluble in water.

It is usually sold as an aqueous solution.

(b) **Heating effect**: When heated at 250°C, it is converted into pyrophosphoric acid.

$$2H_3PO_4 \xrightarrow{250^{\circ}C} H_4P_2O_7 + H_2O$$

On further heating, it is converted into metaphosphoric acid.

$$H_3PO_4 \xrightarrow{\text{Heat } \cdot} HPO_3 + H_2O$$

or

$$H_4P_2O_7 \xrightarrow{\text{Heat}} 2HPO_3 + H_2O$$

When strongly heated at red heat, it forms P<sub>4</sub>O<sub>10</sub>.

$$4H_3PO_4 \longrightarrow P_4O_{10} + 6H_2O$$

(c) Acidic nature: It is a tribasic acid, *i.e.*, all the three hydrogen atoms are ionisable. It forms three series of salts.

$$H_3PO_4 \Longrightarrow H^+ + H_2PO_4^- \Longrightarrow 2H^+ + HPO_4^{2-} \Longrightarrow 3H^+ + PO_4^{3-}$$
 $Na_4PO_4 \longrightarrow Na_2HPO_4 \longrightarrow Na_3PO_4$ 
(Primary salt) (Secondary salt) (Normal or tertiary salt)

Possible sodium salts are sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>), disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>), and trisodium phosphate (Na<sub>3</sub>PO<sub>4</sub>).

Primary salt on heating forms a salt of metaphosphoric acid.

$$\begin{array}{c|c} NaH_2PO_4 & \xrightarrow{\quad Heat \quad} NaPO_3 & + & H_2O \\ \hline Sodium & dihydrogen & Sodium & meta-phosphate \\ \hline phosphate & phosphate \\ \end{array}$$

Secondary salt on heating forms a salt of pyrophosphoric acid.

Normal salt is not affected by heating.

In case, ammonium ion is present in the salt it behaves as hydrogen.

$$2MgNH_4PO_4 \xrightarrow{Heat} Mg_2P_2O_7 + 2NH_3 + H_2O$$
 $NaNH_4HPO_4 \xrightarrow{Heat} NaPO_3 + NH_3 + H_2O$ 

(d) **Reaction with AgNO<sub>3</sub>**: A yellow precipitate of silver phosphate is formed.

$$3AgNO_3 + H_3PO_4 \longrightarrow Ag_3PO_4 + 3HNO_3$$
  
Yellow ppt.

(e) **Reaction with BaCl<sub>2</sub>:** A white precipitate of barium phosphate is formed in neutral or alkaline solution.

$$3BaCl_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 6HCl$$
White ppt.

(f) **Reaction with bromides and iodides:** Hydrobromic and hydroiodic acids are liberated from bromides and iodides respectively. This is the laboratory preparation of HBr and HI.

$$3NaBr + H_3PO_4 \longrightarrow Na_3PO_4 + 3HBr$$
  
 $3NaI + H_3PO_4 \longrightarrow Na_3PO_4 + 3HI$ 

(g) **Reaction with magnesium salt:** Magnesium salts combine with orthophosphoric acid in presence of ammonium chloride and ammonium hydroxide to form a white precipitate of magnesium ammonium phosphate.

$$MgSO_4 + NH_4Cl + H_3PO_4 \longrightarrow Mg(NH_4)PO_4 + H_2SO_4 + HCl$$

This reaction is used to test Mg<sup>2+</sup> ion.

(h) On heating orthophosphoric acid in presence of nitric acid with ammonium molybdate, a canary yellow precipitate of ammonium phosphomolybdate is formed.

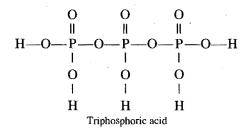
$$H_3PO_4 + 2IHNO_3 + 12(NH_4)_2MoO_4 \longrightarrow$$

$$(NH_4)_3PO_412MoO_3 + 21NH_4NO_3 + 12H_2O$$
Ammonium phosphomolybdate

This reaction is used to test  $PO_4^{3-}$  ion.

(i) Orthophosphoric acid, H<sub>3</sub>PO<sub>4</sub> undergoes condensation reaction to form other phosphoric acids. For example, two orthophosphoric acid molecules condense to form diphosphoric acid or pyrophosphoric acid.

Two series of these phosphoric acids exist (all having in the +5 oxidation state). One series consist of the linear polyphosphoric acids, which are acids with the general formula  $H_{n+2}P_nO_{3n+1}$  formed from linear chains of P—O bonds.



The other series consists of the metaphosphoric acids, which are acids with the general formula  $(HPO_3)_n$ . When a linear polyphosphoric acid chain is very long, the formula becomes  $(HPO_3)_n$ , with n very large, and the acid is called polymetaphosphoric acid.

Sodium triphosphate, Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>, one of the most commonly used polyphosphate, is manufactured by adding sufficient sodium carbonate to orthophosphoric acid to give a solution of the salts NaH<sub>2</sub>PO<sub>2</sub> and Na<sub>2</sub>HPO<sub>4</sub>. When this solution is sprayed into a hot kiln, the orthophosphate ions condense to give sodium triphosphate.

Uses: Orthophosphoric acid is used:

- (a) for making metaphosphoric and polyphosphoric acids.
- (b) for preparation of HBr and HI in the laboratory.
- (c) as a stabilizer for H<sub>2</sub>O<sub>2</sub>.
- (d) for soft drinks.
- (e) for manufacture of phosphate fertilizers.
- (f) Orthophosphoric acid as polyphosphates and metaphosphates are used in detergents, where they act as water softeners by complexing with metal ions in the water.

**Structure:** Orthophosphoric acid is a tribasic acid, *i.e.*, 3 hydroxyl groups are present. The structure of the acid is thus represented as:

Phosphorus atom lies in  $sp^3$  hybrid state.

## (iv) Pyrophosphoric acid, H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>

**Preparation:** It is prepared by heating orthophosphoric acid at 250–260°C.

$$2H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O$$

A pure sample of the acid is formed by heating an equimolecular mixture of orthophosphoric acid and phosphorus oxychloride.

$$5H_3PO_4 + POCl_3 \longrightarrow 3H_4P_2O_7 + 3HCl$$

On cooling at -10°C, crystals of the acid are obtained.

**Properties:** It is a white crystalline solid, soluble in water. In aqueous solution, it is converted into orthophosphoric acid.

$$H_4P_2O_7 + H_2O \longrightarrow 2H_3PO_4$$

On strong heating, it is converted into metaphosphoric acid.

$$H_4P_2O_7 \xrightarrow{\text{Red heat}} 2HPO_3 + H_2O$$

It is a tetrabasic acid and forms two series of salts.

$$H_4P_2O_7 + 2NaOH \longrightarrow Na_2H_2P_2O_7 + 2H_2O$$

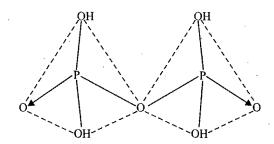
$$H_4P_2O_7\,+\,4NaOH \longrightarrow \,Na_4P_2O_7\,+\,4H_2O$$

It gives a white precipitate with AgNO<sub>3</sub>.

$$4AgNO_3 + H_4P_2O_7 \longrightarrow Ag_4P_2O_7 + 4HNO_3$$

**Structure:** It is a tetrabasic acid, *i.e.*, 4 hydroxyl groups are present. The structure follows directly from the fact that the acid can be prepared by removing one water molecule from two molecules of orthophosphoric acid.

Each phosphorus atom lies in tetrahedral environment. (sp<sup>3</sup> hybrid state.)



## (v) Metaphosphoric acid, HPO<sub>3</sub>

**Preparation:** It is prepared by heating orthophosphoric acid or pyrophosphoric acid or diammonium hydrogen orthophosphate.

$$H_3PO_4 \xrightarrow{600^{\circ}C} HPO_3 + H_2O;$$
 $H_4P_2O_7 \xrightarrow{600^{\circ}C} 2HPO_3 + H_2O$ 
 $(NH_4)_2HPO_4 \longrightarrow HPO_3 + 2NH_3 + H_2O$ 

It is also prepared by dissolving P<sub>2</sub>O<sub>5</sub> with small amount of water at 0°C.

$$P_2O_5 + H_2O \longrightarrow 2HPO_3$$

**Properties:** It is a transparent glassy solid. The acid is, therefore, known as glacial phosphoric acid. It dissolves in water with cracking sound. On boiling the aqueous solution, it is converted into orthophosphoric acid.

$$HPO_3 + H_2O \longrightarrow H_3PO_4$$

It reacts with AgNO<sub>3</sub> forming a white precipitate.

$$AgNO_3 + HPO_3 \longrightarrow AgPO_3 + HNO_3$$

BaCl<sub>2</sub> gives a white precipitate which is insoluble in acetic acid.

$$BaCl_2 + 2HPO_3 \longrightarrow Ba(PO_3)_2 + 2HCl$$

It forms salts with alkalies. The salts are called metaphosphates. Sodium metaphosphate when heated with metal oxides forms mixed phosphates. The mixed phosphates of heavy metals have characteristic colours; hence used in qualitative analysis.

Uses: It is used:

- (i) as a dehydrating agent.
- (ii) as a water softener (calgon) in the form of a polymer, (NaPO<sub>3</sub>)<sub>6</sub>.
  - (iii) in the manufacture of dental cements.

**Structure:** It is a monobasic acid, *i.e.*, it consists one OH group. As it is formed by dehydration of H<sub>3</sub>PO<sub>4</sub>, it can be represented as HO—P=O.

$$\begin{array}{c} OH \\ | \\ HO - P - OH \\ \downarrow \\ O \end{array} \xrightarrow{-H_2O} HO - P = O$$

Metaphosphoric acid or its salts are not present in the form of simple molecules but are often polymerised,  $(HPO_3)_n$ .

Structure of dimeric metaphosphoric acid may be given as:

Structure of trimeric metaphosphoric acid can be represented in cyclic form.

The polymerised form is represented as:

## 4. (i) Phosphorus Trichloride, PCl<sub>3</sub>

**Preparation:** It is formed when dry chlorine is passed over red or white phosphorus heated gently in a retort over a water bath. The vapours of trichloride are condensed in a receiver cooled in a freezing mixture.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

**Properties:** It is colourless fuming liquid. It reacts violently with water forming phosphorus acid.

$$PCl_3 + 3HOH \longrightarrow H_3PO_3 + 3HCl$$

It reacts with concentrated H<sub>2</sub>SO<sub>4</sub> forming chloro-sulphonic acid.

$$4H_2SO_4 + 2PCl_3 \longrightarrow 2HSO_3Cl + P_2O_5 + 2SO_2 + 4HCl + H_2O$$
Chloro-sulphonic

or 
$$2H_2SO_4 + PCl_3 \longrightarrow HSO_3Cl + HPO_3 + SO_2 + 2HCl$$

It reacts with organic compounds containing hydroxyl group.

$$\begin{array}{c} 3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3 \\ \text{Ethyl alcohol} & \text{Ethyl chloride} \end{array}$$

3CH<sub>3</sub>COOH + PCl<sub>3</sub> 
$$\longrightarrow$$
 3CH<sub>3</sub>COCl + H<sub>3</sub>PO<sub>3</sub>  
Acetic acid Acetyl chloride

$$3C_6H_5SO_2\cdot OH + PCl_3 \longrightarrow 3C_6H_5SO_2Cl + H_3PO_3$$
Benzene sulphonic
Benzene sulphonyl
chloride

It directly combines with Cl<sub>2</sub>, O<sub>2</sub> and S. This indicates that it is an unsaturated compound.

$$\begin{array}{c} PCl_3 + Cl_2 \longrightarrow PCl_5 \\ 2PCl_3 + O_2 \longrightarrow 2POCl_3 \\ PCl_3 + S \longrightarrow PSCl_3 \end{array}$$

It acts as a reducing agent.

$$PCl_3 + SO_2Cl_2 \longrightarrow PCl_5 + SO_2$$

$$PCl_3 + SO_3 \longrightarrow POCl_3 + SO_2$$

$$3PCl_3 + SOCl_2 \longrightarrow POCl_3 + PSCl_3 + PCl_5$$

$$3PCl_3 + S_2Cl_2 \longrightarrow PCl_5 + 2PSCl_3$$

It reacts with finely divided metals when hot.

$$12Ag + 4PCl_3 \longrightarrow 12AgCl + P_4$$
  
 $6Na + PCl_3 \longrightarrow 3NaCl + Na_3P$ 

**Uses:** It is used in the manufacture of  $POCl_3$  and in the preparation of organic compounds.

**Structure:** Its structure is similar to ammonia. P atom undergoes  $sp^3$  hybridization. In the tetrahedral configuration, one of the position is occupied by a lone pair. Thus, it is pyramidal in shape.

## (ii) Phosphorus Pentachloride, PCI<sub>5</sub>

**Preparation:** It is obtained by action of an excess of dry chlorine gas on phosphorus trichloride.

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

It may be obtained by the action of sulphuryl chloride (SO<sub>2</sub>Cl<sub>2</sub>) on phosphorus or phosphorus trichloride.

$$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$$
  
 $PCl_3 + SO_2Cl_2 \longrightarrow PCl_5 + SO_2$ 

**Properties:** It is almost colourless crystalline solid with pungent odour when pure. On heating it sublimes at 160°C. When heated it dissociates into PCl<sub>3</sub> and Cl<sub>2</sub>.

$$PCl_5 \Longrightarrow PCl_3 + Cl_2$$

It undergoes hydrolysis violently by water.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$
  
 $PCl_5 + 4H_2O \longrightarrow H_2PO_4 + 5HCl$ 

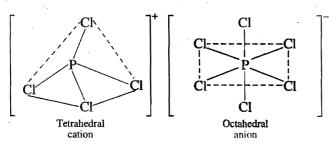
It reacts with hydroxy compounds and replaces hydroxyl groups to chlorine atoms.

$$\begin{array}{c} C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl \\ CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl \\ SO(OH)_2 + 2PCl_5 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl \\ Sulphuric acid \\ \end{array}$$

Many metals are converted into chlorides when heated with PCl<sub>5</sub>.

$$PCl_5 + Zn \longrightarrow ZnCl_2 + PCl_3$$

**Uses:** It is used as chlorinating agent in organic chemistry. **Structure:** X-ray studies have revealed that solid PCl<sub>5</sub> consists of ionic lattices, *i.e.*, tetrahedral [PCl<sub>4</sub>]<sup>+</sup> cations and octahedral [PCl<sub>6</sub>]<sup>-</sup> anions. In vapour state, it has trigonal bipyramid shape in which P has gone  $sp^3d$  hybridization. (See page 99)



# 10.8 ARSENIOUS OXIDE OR ARSENIC TRIOXIDE

This is the most important compound of arsenic and is technically called as white arsenic.

**Preparation:** On a large scale, it is obtained by roasting arsenopyrite ore, FeAsS, in air.

$$2FeAsS + 5O_2 \longrightarrow As_2O_3 + Fe_2O_3 + 2SO_2$$

It is also formed when arsenic is heated in air or oxygen.

$$4As + 3O_2 \longrightarrow 2As_2O_3$$

**Properties:** (a) It is a white poisonous powder. A very small dose of 50 mg or so may prove fatal. It undergoes sublimation.

(b) It is sparingly soluble in water. It reacts with water to form arsenious acid. The oxide is, therefore, known as arsenious anhydride.

$$As_2O_3 + 3H_2O \longrightarrow 2H_3AsO_3$$

The acid is unstable and is known in solution. Its salts, known as arsenites, are quite stable.

(c) It is an amphoteric oxide.

$$As_2O_3 + 6NaOH \longrightarrow 2Na_3AsO_3 + 3H_2O$$
Sodium arsenite
$$As_2O_3 + 6HC1 \longrightarrow 2AsCl_3 + 3H_2O$$
Arsenic chloride

(d) When treated with hydrogen sulphide, arsenic sulphide (yellow precipitate) is formed.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

(e) It acts as a reducing agent as it is changed to pentoxide (or arsenic acid,  $As_2O_5 + 3H_2O \longrightarrow 2H_3AsO_4$ )

(i) 
$$As_2O_3 + 2I_2 + 2H_2O \longrightarrow As_2O_5 + 4HI$$
  
(ii)  $[2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 2$   
 $As_2O_3 + 2O \longrightarrow As_2O_5$   
 $As_2O_3 + 4HNO_3 \longrightarrow As_2O_5 + 4NO_2 + 2H_2O$   
(iii)  $[2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O] \times 2$ 

$$[As_2O_3 + 2O \longrightarrow As_2O_5] \times 5$$

$$4KMnO_4 + 6H_2SO_4 + 5As_2O_3 \longrightarrow$$

$$2K_2SO_4 + 4MnSO_4 + 5As_2O_5 + 6H_2O$$
(iv)
$$[H_2O_2 \longrightarrow H_2O + O] \times 2$$

$$As_2O_3 + 2O \longrightarrow As_2O_5$$

$$As_2O_3 + 2H_2O_2 \longrightarrow As_2O_5 + 2H_2O$$
(v)
$$[O_3 \longrightarrow O_2 + O] \times 2$$

$$As_2O_3 + 2O \longrightarrow As_2O_5$$

$$As_2O_3 + 2O \longrightarrow As_2O_5$$

$$As_2O_3 + 2O \longrightarrow As_2O_5$$

(f) It is reduced to arsenic by acidified stannous chloride.  $[SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2H] \times 3$   $As_2O_3 + 6H \longrightarrow 2As + 3H_2O$  $As_2O_3 + 3SnCl_2 + 6HCl \longrightarrow 3SnCl_4 + 2As + 3H_2O$ 

- **Uses:** (i) It is used as a weed killer and as an insecticide.
- (ii) In very small doses, it is used as medicine and for killing rats.
  - (iii) It is used for making pyrex glass.
  - (iv) As a reducing agent in volumetric analysis.
  - (v) It is employed in dyeing and calicoprinting
  - (vi) It is used for preservation of hides and skins.

## 10 FERTILIZERS

For the normal and healthy growth of plants, more than twelve elements such as carbon, oxygen, hydrogen, nitrogen, phosphorus, potassium, calcium, magnesium, iron, zinc, manganese, molybdenum, sulphur, etc., are essential. These are called plant nutrients. Out of these elements, carbon, hydrogen, oxygen and a part of nitrogen are drawn from the inexhaustible air and water. The remaining elements including nitrogen are supplied by soil. Nitrogen, phosphorus and potassium are regarded as essential plant nutrients and are consumed in large quantities. Other elements are required in minute quantities by plants and are termed as secondary nutrients. The soil is never deficient in secondary nutrients. However, after a few years of continuous cultivation, the soil becomes poorer and poorer in materials supplying nitrogen, phosphorus and potassium to plants. If the soil is not compensated what it has lost in time, it would become less productive and ultimately infertile. Thus, in order to maintain soil fertility, it is necessary to add materials containing nitrogen, phosphorus and potassium in the form of manures. Manures are of two types:

- (1) Natural manures and (2) Artificial manures.
- 1. Natural manures: It includes animal waste such as blood, bones, horns, leather waste, fish scrap, excreta, night soil, sewage, sludge, tankage, guano, etc., and decayed plants such as cotton seed meal, wood or tobacco stem ashes, oil cakes and green growing plants buried in the soil, etc.
- 2. Chemical manures or artificial manures or fertilizers: These are chemical compounds containing nitrogen, phosphorus or potassium obtained by artificial means. These chemical compounds are generally called fertilizers. "The chemical substances which are added to the soil as to make up the deficiency of essential elements are called fertilizers".

Every chemical compound of nitrogen, phosphorus and potassium cannot be used as a fertilizer. The chemical substance which can be used as a fertilizer must have the following characteristics:

- (i) It must be soluble in water.
- (ii) It should be easily assimilated by plants.
- (iii) It should be fairly stable.

- (iv) It should not be injurious to plants.
- (v) It should not disturb pH of the soil.
- (vi) It should be cheap.

### Classification of fertilizers:

Fertilizers are classified according to the elements (N, P and K) which they supply to the soil:

- (i) Nitrogenous fertilizers
- (ii) Phosphatic fertilizers
- (iii) Potash fertilizers
- (iv) Phosphatic cum nitrogen fertilizers
- (v) NPK fertilizers.

## Nitrogenous Fertilizers

The important nitrogenous compounds used as fertilizers are:

- (i) Ammonium nitrate
- (ii) Ammonium sulphate,
- (iii) Calcium cyanamide,
- (iv) Calcium ammonium nitrate,
- (v) Basic calcium nitrate,
- (vi) Urea.

## (i) Ammonium nitrate

Ammonium nitrate is prepared from ammonia. Ammonia from the Haber process is burned in oxygen over a platinum catalyst to obtain niric oxide, NO;

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

The nitric oxide, reacts readily with oxygen from the air to form nitrogen dioxide, NO<sub>2</sub>;

$$2NO + O_2 \longrightarrow 2NO_2$$

NO<sub>2</sub> in turn reacts with water to yield nitric acid HNO<sub>3</sub> and nitrous acid, HNO<sub>2</sub>. The nitrous acid, being unstable, is decomposed with heat and the resulting nitric oxide, NO, can be volatilized and recycled,

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$
  
 $3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$ 

Additional ammonia then reacts with the nitric acid to produce ammonium nitrate  $(NH_4NO_3)$ ;

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3$$

Solid ammonium nitrate should be **handled carefully** though pure ammonium nitrate is quite stable in farming operation, it is an oxidising agent and can explode on heating when mixed in bulk with reducing materials. Pure ammonium nitrate applied to the soil poses no explosive threat at all.

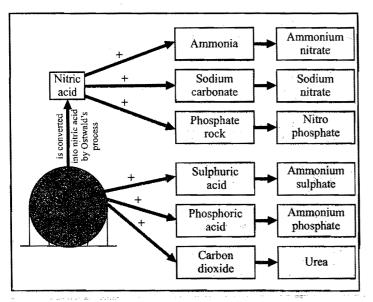


Fig. 10.16 Nitrogen fertilizers from anhydrous ammonia

## (ii) Ammonium sulphate, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

The following two processes are used for its manufacture:

(a) Ammonia liquor obtained from dry distillation of coal: Ammonia liquor obtained during distillation of coal consists various ammonium compounds. In order to recover ammonia, the liquor is mixed with lime and heated in stills by steam. The mixture of ammonia and steam so produced is passed through a lead lined tank containing 60% H<sub>2</sub>SO<sub>4</sub>, when crystals of  $(NH_4)_2SO_4$  separate on cooling.

$$(NH_4)_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NH_3 + 2H_2O$$
  
 $2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$ 

$$\begin{array}{c} \text{NH}_4\text{HS} \xrightarrow{\text{Heat}} \text{NH}_3 + \text{H}_2\text{S} \\ 2\text{NH}_3 + \text{H}_2\text{SO}_4 \longrightarrow (\text{NH}_4)_2\text{SO}_4 \end{array}$$

(b) Ammonia obtained from Haber process: The synthetic ammonia obtained from Haber process is also converted into ammonium sulphate by absorbing it in sulphuric acid.

## Sindri process

Ammonium sulphate is manufactured at Sindri (Jharkhand) by passing synthetic ammonia into a suspension of finely powdered CaSO<sub>4</sub> (Gypsum) in water through which a stream of carbon dioxide is also passed.

$$2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$$
  
 $CaSO_4 + (NH_4)_2CO_3 \longrightarrow (NH_4)_2SO_4 + CaCO_3$ 

The insoluble CaCO<sub>3</sub> is filtered off. The solution on evaporation under vacuum and cooling yields crystals of ammonium sulphate. Ammonium sulphate is generally called Sindri fertilizer in India.

Ammonium sulphate contains 24–25% ammonia. This ammonia cannot be easily utilised by plants. It is converted into nitrates by nitrifying bacteria in the soil and nitrates are taken up easily by plants from the soil. It should not be frequently used otherwise the soil becomes acidic. It should be generally used after the seeds have germinated.

$$(NH_4)_2SO_4 \xrightarrow[compounds in soil]{Basic} NH_3 \xrightarrow[bacteria]{Nitrifying} Nitrates$$

## (iii) Calcium cyanamide, CaCN<sub>2</sub> (Nitrolim)

It is manufactured by heating calcium carbide with nitrogen at 1100°C in an electric furnace. The product is usually dark grey in colour due to the presence of graphite and is sold in the market in the name of nitrolim.

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$
Calcium
cyanamide

In soil, it is converted into urea which then decomposes into ammonia. Ammonia is finally converted into nitrates by nitrifying bacteria

$$CaCN_2 + H_2O + CO_2 \longrightarrow CN \cdot NH_2 + CaCO_3$$

$$CN \cdot NH_2 + H_2O \longrightarrow CO(NH_2)_2$$

$$Urea$$

$$CO(NH_2)_2 + H_2O \longrightarrow 2NH_3 + CO_2$$

It is a slow fertilizer and its effects on fertility are of more permanent nature. It is added to the soil before sowing and not when the plants are actually growing.

## (iv) Calcium ammonium nitrate, Ca(NO<sub>3</sub>)<sub>2</sub>·NH<sub>4</sub>NO<sub>3</sub> (CAN)

It is known as Nangal fertilizer in India. Ammonia is obtained by Haber process. A part of ammonia is converted into nitric acid by Ostwald's process. Excess of nitric acid and ammonia are then made to react with each other to give ammonium nitrate.

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

The solution is concentrated and treated with powdered limestone as to neutralise the free acid present in the solution.

$$2HNO_3 + CaCO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2$$
  
 $Ca(NO_3)_2 + NH_4NO_3 \longrightarrow Ca(NO_3)_2 \cdot NH_4NO_3$   
 $CAN$ 

CAN is hygroscopic. The pellets are, therefore, coated with calcium silicate as to protect from moisture. Ammonium nitrate is explosive but CAN does not explode. This fertilizer is superior to ammonium sulphate as it is more soluble in water and does not make the soil acidic.

## (v) Basic calcium nitrate, Ca(NO<sub>3</sub>)<sub>2</sub>·CaO

It is formed by reacting limestone with nitric acid.

$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2$$
  
It is then mixed with lime.  
 $Ca(NO_3)_2 + CaO \longrightarrow Ca(NO_3)_2 \cdot CaO$ 
Basic calcium nitrate

Being highly deliquescent, it is packed in water proof bags. Basic calcium nitrate is also called **Norwegian saltpetre** or **nitrate of lime.** It is preferred to the normal calcium nitrate as a fertilizer since it is less deliquescent.

## (vi) Urea, NH2CONH2

Urea is one of the world's most important chemicals because of its wide use as fertilizer.

It is manufactured by reacting ammonia and carbon dioxide under high atmospheric pressure near 200°C. Ammonium carbamate (NH<sub>2</sub>COONH<sub>4</sub>) formed as an intermediate product changes into urea.

A slurry of water, urea and ammonium nitrate is often applied to crops under the name of "liquid nitrogen". Such a solution can contain upto 30% nitrogen and is easy to store and apply. When applied to the surface of the ground around plants urea is subjected to considerable nitrogen loss. When urea hydrolyses (is decomposed by water) ammonia is formed, out of it some ammonia is lost to the air and some is absorbed by moist soil particles. As much as half of the nitrogen applied can be lost in this way.

Out of the nitrogen fertilizers, urea has the highest nitrogen content equal to 46.6%. It has no explosive property and there is no risk in the storage. It does not alter the pH of the soil. It can be used for all types of crops. However, there is one disadvantage, urea is not so stable as other nitrogenous fertilizers. It decomposes even at lower temperatures in humid atmosphere. It is highly soluble in water and hence requires airtight packing.

Note: Inorganic nitrate fertilizers are water soluble and contribute significantly to nitrate pollution in the ground water of farming regions. Since excess nitrates in drinking water and food supplies cause blood disorders and contribute to the formation of carcinogenic nitrosoamines\*, the present opinion is to keep the nitrate out of the ground water or to remove it in the purification of drinking water.

## Phosphatic Fertilizers

The minerals of phosphorus such as phosphorite,  $[Ca_3(PO_4)_2]$  and apatite,  $[3Ca_3(PO_4)_2 \cdot CaF_2]$  are sparingly

soluble in water and thus do not serve as source of phosphorus for plants. These are, therefore, converted into soluble materials which can act as good fertilizers.

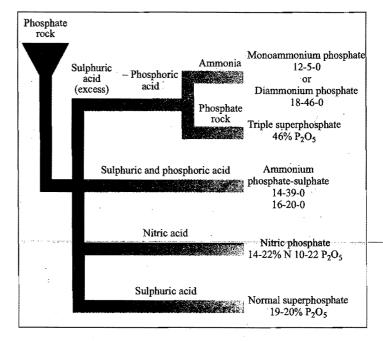


Fig. 10.17 Phosphatic fertilizers from phosphate rock

The important phosphatic fertilizers are:

- (i) Calcium superphosphate
- (ii) Nitrophosphate
- (iii) Triple phosphate
- (iv) Phosphatic slag

## (i) Calcium superphosphate or superphosphate of lime Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O + 2(CaSO<sub>4</sub>·2H<sub>2</sub>O)

Calcium phosphate, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, is not very useful to a growing plant because of its very low solubility. When calcium phosphate is treated with sulphuric acid it becomes more soluble and is called "superphosphate".

$$\begin{array}{c} Ca_{3}(PO_{4})_{2} + 2H_{2}SO_{4} \longrightarrow \underbrace{Ca(H_{2}PO_{4})_{2} + 2CaSO_{4}}_{Superphosphate} \\ \end{array}$$

It is prepared on a large scale by treating phosphorite or bone ash with calculated quantity of 70% H<sub>2</sub>SO<sub>4</sub>.

$$Ca_{3}(PO_{4})_{2} + 2H_{2}SO_{4} + 5H_{2}O \longrightarrow$$

$$Ca(H_{2}PO_{4})_{2} \cdot H_{2}O + 2CaSO_{4} \cdot 2H_{2}O$$

$$Ca(H_{2}PO_{4})_{2} \cdot H_{2}O + 2CaSO_{4} \cdot 2H_{2}O$$

Superphosphate of lime has 16-20% of P2O5.

<sup>\*</sup>Carcinogens are chemicals, that cause cancer.

## (ii) Nitrophosphate

It is prepared in the same way as superphosphate from phosphorite mineral using nitric acid instead of sulphuric acid.

$$Ca_3(PO_4)_2 + 4HNO_3 \longrightarrow \underbrace{Ca(H_2PO_4)_2 + 2Ca(NO_3)_2}_{Nitrophosphate or}$$

The advantage of this fertilizer is that in addition to phosphorus, it contains nitrogen as well. Thus, this is a mixed fertilizer.

## (iii) Triple superphosphate of lime

This is another form of superphosphate. It is obtained by the action of orthophosphoric acid, H<sub>3</sub>PO<sub>4</sub> (70%) with phosphate mineral.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \longrightarrow 3Ca(H_2PO_4)_2$$

Triple phosphate has calcium hydrogen phosphate but it does not have calcium sulphate that is why percentage of  $P_2O_5$  in triple superphosphate in about three times to calcium superphosphate, and hence called **triple superphosphate**. It has about 42-46% of  $P_2O_5$ .

## (iv) Phosphatic slag or Thomas slag:

It is a by-product of steel industry. When iron ore is burnt with limestone in the presence of air, calcium phosphate and calcium silicate appear as slag.

$$\begin{array}{ccc} 4P + 5O_2 & \longrightarrow & P_4O_{10} \\ 6CaO + P_4O_{10} & \longrightarrow & 2Ca_3(PO_4)_2 \\ CaO + SiO_2 & \longrightarrow & CaSiO_3 \end{array} \right\} Thomas slag$$

The slag being lighter rises on the top of molten metal and is easily separated. It is cooled. The solid mass thus obtained is ground to a fine powder and used as fertilizer. It has 14-18% of  $P_2O_5$ .

#### Potash Fertilizers

Potassium nitrate, potassium chloride and potassium sulphate are used as fertilizers.

#### NPK Fertilizers

Fertilizers containing N, P and K in suitable adjusted proportions are known as NPK fertilizers. These are obtained by mixing nitrogenous, phosphatic and potash fertilizers in suitable proportions. Expression like 4–8–2 used for a mixed fertilizer indicates that it contains 4% N<sub>2</sub>, 8% P<sub>2</sub>O<sub>5</sub> and 2% K<sub>2</sub>O.

In India, plants for the manufacture of fertilizers are established/situated at,

- 1. Sindri (Jharkhand)
- 2. Trombay (Maharashtra)
- 3. Nangl (Punjab)
- 4. Rourkela (Orissa) and
- 5. Namroop (Assam)

# SOME SOLVED PROBLEMS

**Example 1.** Complete and balance the following reactions:

- (i) Copper reacts with HNO<sub>3</sub> to give NO and NO<sub>2</sub> in molar ratio of 2:1. [I.I.T. 1992]
- (ii) Red phosphorus is reacted with iodine in presence of water. [I.I.T. 1992]
- (iii) Ammonium sulphate is heated with a mixture of nitric oxide and nitrogen dioxide.
- (iv) White phosphorus is boiled with a strong solution of sodium hydroxide in an inert atmosphere. [I.I.T. 1993]
- (v) The preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide. [I.I.T. 1990]
- (vi) Nitrogen is obtained by the reaction of ammonia with KMnO<sub>4</sub>. [I.I.T. 1991]
- (vii) Aqueous solution of sodium nitrate is heated with zinc dust and caustic soda. [L.J.T. 1990]
- (viii) Phosphorus reacts with conc. HNO<sub>3</sub> to give phosphoric acid. [I.I.T. 1991]
- (ix) The preparation of phosphine from CaO and white phosphorus. [1.I.T. 1990]
- (x) Sodium nitrite is produced by absorbing oxides of nitrogen in aqueous solution of sodium carbonate. [I.I.T. 1991]

#### **Solution:**

(i) 
$$2HNO_3 \longrightarrow 2NO + H_2O + 3O$$
  
 $3Cu + 3O + 6HNO_3 \longrightarrow 3Cu(NO_3)_2 + 3H_2O$   
 $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O...(i)$   
 $2HNO_3 \longrightarrow 2NO_2 + H_2O + O$   
 $Cu + O + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$   
 $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O...(ii)$ 

To get NO and  $NO_2$  in the ratio of 2:1, the eqn. (i) be multiplied by two and added in eqn. (ii).

7Cu + 20HNO<sub>3</sub> 
$$\longrightarrow$$
 7Cu(NO<sub>3</sub>)<sub>2</sub> + 4NO + 2NO<sub>2</sub> + 10H<sub>2</sub>O  
(ii) 2P + 3I<sub>2</sub>  $\longrightarrow$  2PI<sub>3</sub>  
2PI<sub>3</sub> + 3H<sub>2</sub>O  $\longrightarrow$  H<sub>3</sub>PO<sub>3</sub> + 3HI  
(iii) NO + NO<sub>2</sub>  $\longrightarrow$  N<sub>2</sub>O<sub>3</sub>  
(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>  $\longrightarrow$  2NH<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>  
2NH<sub>3</sub> + N<sub>2</sub>O<sub>3</sub>  $\longrightarrow$  2N<sub>2</sub> + 3H<sub>2</sub>O  
(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + NO + NO<sub>2</sub>  $\longrightarrow$  2N<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub> + 3H<sub>2</sub>O

(iv) 
$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$$
Sodium hypophosphite

(v)  $2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$ 
 $CaSO_4 + (NH_4)_2CO_3 \longrightarrow (NH_4)_2SO_4 + CaCO_3$ 
(vi)  $2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3O$ 
 $2NH_3 + 3O \longrightarrow N_2 + 3H_2O$ 

$$2KMnO_4 + 2NH_3 \longrightarrow 2KOH + 2MnO_2 + N_2 + 2H_2O$$
(vii)  $[Zn + 2NaOH \longrightarrow Na_2ZnO_2 + 2H] \times 4$ 
 $NaNO_3 + 8H \longrightarrow NaOH + NH_3 + 2H_2O$ 

$$4Zn + 7NaOH + NaNO_3 \longrightarrow NH_3 + 4Na_2ZnO_2 + 2H_2O$$
(viii)  $[2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 10$ 
 $P_4 + 10O + 6H_2O \longrightarrow 4H_3PO_4$ 

$$P_4 + 2OHNO_3 \longrightarrow 4H_3PO_4 + 2ONO_2 + 4H_2O$$
(ix)  $[CaO + H_2O \longrightarrow Ca(OH)_2] \times 3$ 
 $8P + 3Ca(OH)_2 + 6H_2O \longrightarrow 3Ca(H_2PO_2)_2 + 2PH_3$ 
 $8P + 3CaO + 9H_2O \longrightarrow 3Ca(H_2PO_2)_2 + 2PH_3$ 
(x)  $Na_2CO_3 + NO + NO_2 \longrightarrow 2NaNO_2 + CO_2$ 

#### **Example 2.** Answer the following:

- (i) Why concentrated  $H_2SO_4$ , anhydrous  $CaCl_2$  or  $P_4O_{10}$  cannot be used as dehydrating agents for ammonia?
- (ii) Why nitrous oxide supports combustion more vigorously than air?
- (iii) Why red phosphorus is denser and chemically less reactive than white phosphorus?
- (iv) Nitric acid acts as oxidising agent while nitrous acid can act both as an oxidising and a reducing agent.
  - (v) Why commercial nitric acid is generally yellow in colour? **Solution:**
- (i) Conc.  $H_2SO_4$ , anhydrous  $CaCl_2$  and  $P_4O_{10}$  directly react with ammonia.

$$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$$

$$CaCl_2 + 8NH_3 \longrightarrow CaCl_2 \cdot 8NH_3$$

$$P_4O_{10} + 12NH_3 + 6H_2O \longrightarrow 4(NH_4)_3PO_4$$

(ii) Air has oxygen about 1/5th of the volume while  $N_2O$  on decomposition produces oxygen about 1/3rd of the volume.

Air 
$$\longrightarrow$$
 4 vol.  $N_2 + 1$  vol.  $O_2$ ;  $O_2 = \frac{\text{Total volume}}{5}$   
 $2N_2O \longrightarrow 2N_2 + O_2$ ;  $O_2 = \frac{\text{Total vol. of } N_2 \text{ and } O_2}{3}$ 

- (iii) Red phosphorus is regarded as a polymer consisting of chains of P<sub>4</sub> tetrahedra linked together. This makes red phosphorus denser and less reactive.
- (iv) In HNO<sub>3</sub>, the oxidation state of nitrogen is +5. Nitrogen can only be converted into lower oxidation states as +5 state

is the highest. Thus, it acts only as an oxidising agent. In nitrous acid,  $HNO_2$ , nitrogen is in +3 oxidation state. Thus, it can be lowered or raised. Hence,  $HNO_2$  acts both as an oxidising and a reducing agent.

(v) Nitrogen dioxide is present in HNO<sub>3</sub> which imparts yellow colour to the nitric acid. NO<sub>2</sub> is usually formed by decomposition of HNO<sub>3</sub> in sunlight.

$$4HNO_3 \xrightarrow{Sunlight} 4NO_2 + 2H_2O + O_2$$

**Example 3.** Explain the following with proper reason:

- (i) Nitrogen is a gas while other members of Vth group are solids.
- (ii) A bottle of liquor ammonia should be cooled before opening.
  - (iii) Ammonia has a higher boiling point than phosphine.
    [M.L.N.R. 1993]
  - (iv)  $PF_5$  is known but  $NF_5$  is not. [M.L.N.R. 1992]
- (v) The experimentally determined N—F bond length in  $NF_3$  is greater than the sum of single bond covalent radii of N and F. [LLT. 1995]

#### **Solution:**

- (i) The nitrogen atom is small in size. It can undergo lateral overlapping forming multiple bonds, *i.e.*, nitrogen molecule consists one sigma and two  $\pi$ -bonds (N=N). The discrete molecules are held together by weak van der Waals' forces. Thus, nitrogen is a gas. As the size increases, the lateral overlap is not strong and multiple bonds are not formed. Four atoms link together by single covalent bonds in tetrahedral form. The molecular masses become high and hence the rest of the members of Vth group are solids.
- (ii) Liquor ammonia has high vapour pressure at room temperature. It is cooled before opening as to reduce the vapour pressure inside the bottle in order to prevent bumping.
- (iii) Nitrogen being more electronegative, hydrogen bonding is observed in ammonia, *i.e.*, association of molecules occurs through hydrogen bonding. This property is absent in phosphine.
- (iv) Nitrogen cannot extend its valency from 3 to 5 due to absence of *d*-orbitals while phosphorus shows pentacovalency as *d*-orbitals are present in it.
- (v) The bond length is high due to repulsion of the bonded pair by both nitrogen and fluorine atoms. This is due to their smaller size and high electron density.
- **Example 4.** A colourless inorganic salt (A) decomposes completely at about 250°C to give only two products (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in this process.

[I.I.T. 1996]

#### Solution:

Both (B) and (C) are neutral oxides. (B) helps in the combustion of white phosphorus. Thus, (B) can be nitrous oxide,  $N_2O$ . (A) is liquid at room temperature, thus it can be water,  $H_2O$ .

The inorganic salt (A) is ammonium nitrate,  $NH_4NO_3$  which on decomposition gives  $N_2O$  and  $H_2O$ .

$$\begin{array}{ccc} NH_4NO_3 & \longrightarrow & N_2O + 2H_2O \\ (A) & (B) & (C) \\ \hline \\ 10N_2O + P_4 & \longrightarrow & P_4O_{10} + 10N_2 \\ & & \\ & & \\ Dehydrating \\ & agent \end{array}$$

**Example 5.** -An aqueous solution of a gas (X) shows following reactions:

- (i) It turns red litmus blue.
- (ii) When added in excess to a copper sulphate solution, a deep blue colour is obtained.
- (iii) On addition to ferric chloride solution a brownish precipitate soluble in HNO<sub>3</sub> is obtained.

Identify (X) and give equations for the reactions in step (ii) and (iii). [Roorkee 1991]

#### Solution:

The gas (X) is  $NH_3$ .

Its aqueous solution is  $NH_4OH$  which turns red litmus to blue.

Step (ii)

$$FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 + 3NH_4Cl$$

$$Fe(OH)_3 + 3HNO_3 \longrightarrow Fe(NO_3)_3 + 3H_2O$$

$$Soluble$$

**Example 6.** Give the names and formulae of the compounds described below:

- (a) A chromium compound which on heating gives nitrogen and an oxide of chromium.
- (b) A compound of N, H and O which is used as a freezing salt and decomposes on heating giving a neutral oxide of nitrogen.
- (c) A compound of N, H, C and O which is used as a fertilizer.

#### **Solution:**

(a) Chromium compound is ammonium dichromate,  $(NH_4)_2Cr_2O_7$ .

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$

(b) The compound is ammonium nitrate, NH<sub>4</sub>NO<sub>3</sub>.

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$
Neutral oxide

(c) The compound is urea, NH<sub>2</sub>CONH<sub>2</sub>.

### **Example 7.** Answer the following:

- (a) Why elemental phosphorus does not exist as  $P_2$  like  $N_2$ ?
- (b) How  $NO_3^-$  and  $PO_3^-$  ions are differ structurally?
- (c) NCl<sub>3</sub> gets readily hydrolysed while NF<sub>3</sub> does not, why?
- (d) Oxides of nitrogen have open chain structures while those of phosphorus have closed chain or cage structures. Why is it so? Illustrate with one structural example for each type of the oxides.

#### Solution:

- (a) Nitrogen because of small size has a tendency to form multiple bonds and thus exist as a diatomic molecule,  $N \equiv N$ . Phosphorus has a comparatively larger size and it has no tendency to form multiple bonds and thus does not form diatomic molecule,  $P \equiv P$ . However, it prefers to form  $P_4$  molecules in which each P is linked to three other P atoms by three single covalent bonds and four P atoms lie at the corners of a regular tetrahedron.
- (b)  $NO_3$  ion exists as a free ion. It has trigonal planar shape as N is in  $sp^2$  hybridized state.

 $PO_3^-$  ion does not exist as free ion but in the polymeric form in which various  $PO_3^-$  units are linked through P-O-P bonds to form either linear or cyclic structures. The P is in  $sp^3$  hybridized state.

- (c) In NCl<sub>3</sub>, Cl has vacant *d*-orbitals to accept lone pair of electrons from oxygen atom of H<sub>2</sub>O molecule. Thus, hydrolysis is possible. In NF<sub>3</sub>, no *d*-orbitals are present.
- (d) Nitrogen on account of small size and high electronegativity has a strong tendency to form multiple bonds ( $p\pi p\pi$  bonds) with oxygen and form oxides with open chain structures. Phosphorus has no tendency to form  $p\pi p\pi$  bonds with oxygen due to its large size and prefers to form single bonds. As a result, closed chain or cage structure results.

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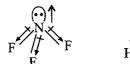
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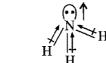
**Example 8.** (a)  $NF_3$  does not have donor properties like ammonia. Explain.

- (b) PCl<sub>5</sub> acts as a chlorinating agent in organic reactions. Give reason.
- (c)  $PCl_5$  exists as  $[PCl_4]^+$   $[PCl_6]^-$  but  $PBr_5$  exists as  $[PBr_4]^+Br^-$ . Explain.

#### **Solution:**

(a) NF<sub>3</sub> has a pyramidal shape like NH<sub>3</sub> with one lone pair of electrons on N-atom.





The lone pair on N is in opposite direction to the N—F bond moments and therefore, it has a very little dipole moment. Thus, lone pair is not very effective and does not show donor properties. However, NH<sub>3</sub> has high dipole moment because its lone pair is in the same direction as the N—H bond moments. Electron density is high and thus, donor properties are observed.

- (b) The structure of PCl<sub>5</sub> is trigonal bipyramid. The axial P—Cl bonds are slightly larger than the equatorial P—Cl bonds. The molecule is, thus, less stable. It breaks upto lose two chlorine atoms present on axial positions and, thus, acts as a chlorinating agent.
- (c) The formation of both PCl<sub>5</sub> and PBr<sub>5</sub> is due to  $sp^3d$ -hybridization of phosphorus, *i.e.*, both have a trigonal bipyramidal geometry which is not a regular structure and, thus, is not very stable. To attain more stable structure, PCl<sub>5</sub> splits up into tetrahedral and octahedral structures.

$$2PCl_5 \Longrightarrow [PCl_4]^+ [PCl_6]^-$$
Tetrahedral Octahedral

But  $PBr_5$  does not split up in the same fashion. The anion  $[PBr_6]^-$  is not possible due to large size of Br atoms.  $PBr_5$ , therefore, splits up into stable tetrahedral structure as,

$$PBr_5 \Longrightarrow [PBr_4]^+Br^-$$
Tetrahedral

**Example 9.** (a) Can  $PCl_5$  act as an oxidising as well as a reducing agent? Justify.

- (b) Give the disproportionation reaction of  $H_3PO_3$ .
- (c) The HNH angle value is higher than HPH, HAsH and HSbH angles. Why?
- (d) Why  $NH_3$  is basic while  $BiH_3$  is only feebly basic? Explain.

#### Solution:

(a) Phosphorus can exhibit a maximum oxidation state of +5. In PCl<sub>5</sub>, the oxidation state of phosphorus is +5. Thus, it cannot increase its oxidation state beyond +5 and consequently it is unable to act as a reducing agent. However, it can act as an oxidising agent by undergoing decrease in oxidation state. For example,

$$PCl_5 + H_2 \longrightarrow PCl_3 + 2HCl$$
 $+5 + 3$ 
 $PCl_5 + Sn \longrightarrow 2PCl_3 + SnCl_4$ 

(b)  $H_3PO_3$  on heating is converted into  $H_3PO_4$  (oxidation state +5) and  $PH_3$  (oxidation state -3). Thus, this is a disproportionation reaction.

- (c) In all the hydrides of group 15 elements, the central atom undergoes  $sp^3$ -hybridisation. The three hybrid orbitals form sigma bonds with three hydrogen atoms and the fourth contains a lone pair of electrons. The lone pair-bond pair repulsions are larger than bond pair-bond pair repulsion. In ammonia both forces are equally present in opposite directions, hence the bond angle decreases from 109°28′ to 107°5′. However, as we go from N to Sb, the size increases and the repulsions between bond pair—bond pair go on decreasing and thus the bond angles keep on decreasing from NH<sub>3</sub> to SbH<sub>3</sub>.
- (d) The central atoms in both NH<sub>3</sub> and BiH<sub>3</sub> contain a lone pair of electrons and thus, both should behave as Lewis bases. But the size of Bi atom is much larger than the nitrogen atom. The electron density on nitrogen atom is much higher in comparison to Bi atom. Consequently, the tendency to donate the electron pair by N in NH<sub>3</sub> is much higher than the tendency of Bi in BiH<sub>3</sub>. Therefore, NH<sub>3</sub> is basic while BiH<sub>3</sub> is feebly basic.

**Example 10.** Illustrate, how does copper metal give different products on reaction with HNO<sub>3</sub>.

#### **Solution:**

Nitric acid acts as an oxidising agent as well as an acid when it reacts with copper. Dilute HNO<sub>3</sub> evolves nitric oxide while concentrated HNO<sub>3</sub> gives nitrogen dioxide.

$$2HNO_{3} \text{ (Dilute)} \longrightarrow H_{2}O + 2NO + 3[O]$$

$$[Cu + O \longrightarrow CuO] \times 3$$

$$[CuO + 2HNO_{3} \longrightarrow Cu(NO_{3})_{2} + H_{2}O] \times 3$$

$$3Cu + 8HNO_{3} \text{ (Dilute)} \longrightarrow 3Cu(NO_{3})_{2} + 2NO + 4H_{2}O$$

$$2HNO_{3} \text{ (Conc.)} \longrightarrow H_{2}O + 2NO_{2} + [O]$$

$$Cu + O \longrightarrow CuO$$

$$CuO + 2HNO_{3} \longrightarrow Cu(NO_{3})_{2} + H_{2}O$$

$$Cu + 4HNO_{3} \longrightarrow Cu(NO_{3})_{2} + 2NO_{2} + 2H_{2}O$$

# **SUMMARY AND IMPORTANT POINTS TO REMEMBER**

- 1. VA or 15th group of the periodic table consists of six elements—nitrogen, phosphorus, arsenic, antimony, bismuth and ununpentium. These elements are collectively known as **pnictogens** and their compounds **pnictides**.
- 2. These are p-block elements as the last differentiating electron is accommodated on np shell. They have general configuration of  $ns^2np^3$  configuration. All the p-orbitals of the outer shell are singly occupied.

$$\begin{array}{ccc}
ns & np \\
\downarrow\uparrow & \uparrow & \uparrow & \uparrow
\end{array}$$

These elements are not so reactive as half filled orbitals are present which are fairly stable. Nitrogen behaves as a noble element under ordinary conditions.

3. VA group is a mixed group of metals, metalloids and non-metals. Metallic nature increases as the atomic number increases.

Nitrogen and phosphorus combine with electropositive elements and form nitrides and phosphides. Bismuth and antimony form alloys.

- 4. Nitrogen is a gas, the phosphorus is a waxy solid and can pass into vapour state readily. The remaining elements are solids and possess metallic lustre.
  - Nitrogen is a diatomic molecule,  $N \equiv N$ . The molecule has one sigma and two  $\pi$ -bonds. The dissociation energy is very large (225 kcal mol<sup>-1</sup>) and thus, is a stable and inert under ordinary conditions.
  - P, As and Sb all exist as discrete tetratomic tetrahedral molecules, viz., P<sub>4</sub>, As<sub>4</sub> and Sb<sub>4</sub> as these are not capable of forming multiple bonds. The angle between X—X—X is 60°.
- 5. In VA or 15th group:
  - (a) density of the elements increases down the group.
  - (b) melting points increase from nitrogen to As and then decreases from As to Bi.
    - The lower values are due to formation of three covalent bonds instead of five covalent bonds due to inert pair effect.
  - (c) atomic radii increase down the group.
  - (d) ionisation energy decreases regularly on moving down the group.
    - The ionisation energy of N is very high due to small size.
  - (e) electronegativity decreases gradually on moving down the group.
  - (f) all the elements except bismuth show allotropy.
  - (g) N, P and As exhibit the property of catenation but this property is much less than IVA elements.
- 6. All the members can show +5 oxidation state toward oxygen. Nitrogen and phosphorus generally exhibit -3 oxidation state due to high electronegativity. +3 oxidation state is observed when only p electrons are used. Its stability increases due to inert pair effect.
  - Nitrogen besides -3, +3 and +5 oxidation states, exhibits a large number of oxidation states from -3 to +5. -3 in NH<sub>3</sub>, -2 in NH<sub>2</sub>·NH<sub>2</sub>, -1 in NH<sub>2</sub>OH, 0 in N<sub>2</sub>, +1 in N<sub>2</sub>O, +2 in NO, +3 in N<sub>2</sub>O<sub>3</sub>, +4 in N<sub>2</sub>O<sub>4</sub> or NO<sub>2</sub> and +5 in N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub>.
- 7. These elements attain stable configuration by forming three covalent bonds. Except nitrogen, all other elements have *d*-orbitals in the valence shell. As a result, one of the two *ns*-electrons may be promoted to *nd*-orbitals to have five unpaired orbitals in the valence shell. These can be utilised to form five bonds. However, nitrogen can show a maximum covalency of 4 when it donates the *ns*-electron pair to Lewis acids.
  - Sb and Bi can lose three electrons to form  $M^{3+}$  ions. Both SbF<sub>3</sub> and BiF<sub>3</sub> are ionic solids.  $M^{3+}$  ions are not stable in solution. They are rapidly hydrolysed as SbO<sup>+</sup> and BiO<sup>+</sup> ions. However,  $M^{3+}$  ions are stable in strong acids.
- **8.** Nitrogen is found in free as well as combined state. It forms 75% by mass and 78% by vol. of atmosphere. In combined state, it occurs as nitrates, proteins and amino acids. Phos-

- phorus is eleventh most abundant element in combined state. It is never found free in nature. P is essential for life of both animals and plants. It is present in DNA, RNA, ADP, ATP, etc. As, Sb and Bi are not abundant.
- 9. Nitrogen is chemically inert under ordinary conditions as it has very high dissociation energy. At high temperatures, it can react with other elements. Phosphorus (white form) is extremely reactive. The strained structure of P<sub>4</sub> is responsible for this. The heavier elements are less reactive.
  - Only nitrogen in this group is capable of forming  $p\pi$ - $p\pi$  multiple bonds within itself and with carbon, oxygen, etc., on account of small size. Phosphorus and other members do not form  $p\pi$ - $p\pi$  multiple bonds but they show multiple bonding of  $d\pi$ - $p\pi$ .
- 10. (a) Oxides of type  $X_2O_3$ ,  $X_2O_4$  and  $X_2O_5$  are formed by the elements of group 15.
  - (b) Greater is the electronegativity more is the acidic nature of its oxides.
  - (c) Acidic nature of each type decreases from N to Bi.

(However, it shows feeble acidic character with strong alkali.)

Acidic nature of  $M_2O_4$  oxides also decreases from  $N_2O_4$  to  $Bi_2O_4$ .

- (d) Thermal stability decreases in each series from N to Bi.
- (e) In the oxides of a particular element, the acidic nature increases as the percentage of oxygen increases or the oxidation state increases.
- 11. (a) All the members of group 15 form oxyacids or oxoacids.
  - (b) The oxyacids of nitrogen are: hyponitrous acid (H<sub>2</sub>N<sub>2</sub>O<sub>2</sub>), nitroxylic acid (H<sub>2</sub>N<sub>2</sub>O<sub>4</sub>), nitrous acid (HNO<sub>2</sub>), nitric acid (HNO<sub>3</sub>), peroxynitric acid (HNO<sub>4</sub>).
    - Nitrous acid is unstable, weak monobasic acid, forms stable salts. This acts as an oxidising and a reducing agent. Nitric acid is a stable, strong monobasic acid. It is a strong oxidising agent.
    - (c) Phosphorus forms two types of oxyacids, one having P in +1 or +3 oxidation state, *i.e.*, phosphorus acids and other having P in +4 or +5 oxidation state, *i.e.*, phosphoric acids. Phosphorus acids act as reducing agents as they tend to disproportionate. The important oxyacids of phosphorus are: hypophosphorus acid (H<sub>3</sub>PO<sub>2</sub>), phosphorus acid (H<sub>3</sub>PO<sub>3</sub>), orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>), metaphosphoric acid (HPO<sub>3</sub>), hypophosphoric acid (H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>) and pyrophosphoric acid (H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>). The number of OH group or groups in oxoacids of phosphorus decides the basicity of the acid.

Acid  $H_3PO_2$   $H_3PO_3$   $H_3PO_4$   $HPO_3$   $H_4P_2O_6$   $H_4P_2O_7$  Basicity 1 2 3 1 4 4 Each oxoacid of phosphorus contains at least one P=O unit and one P—OH unit.

- (d) Arsenic forms two oxyacids—arsenious acid (H<sub>3</sub>AsO<sub>3</sub>) and arsenic acid (H<sub>3</sub>AsO<sub>4</sub>). Antimony forms only one acid H<sub>3</sub>SbO<sub>3</sub>. Bismuth also forms one stable oxoacid, HBiO<sub>3</sub> meta-bismuthic acid.
- (e) The strength and stability of oxoacids having the element in same oxidation state decreases down the group.
- 12. All the members of this group form hydrides of the type  $MH_3$ .
  - (a) All the hydrides are colourless gases.
  - (b) Their smell becomes more and more disagreeable from N to Bi.
  - (c) The poisonous nature increases from NH<sub>3</sub> to BiH<sub>3</sub>.
  - (d) NH<sub>3</sub> is highly soluble in water but other hydrides are less soluble.
  - (e) The basic character decreases from NH<sub>3</sub> to BiH<sub>3</sub>.
  - (f) Thermal stability decreases from NH<sub>3</sub> to BiH<sub>3</sub>. BiH<sub>3</sub> decomposes at room temperature.
  - (g) The reducing nature increases. This shows *M*—H bond strength decreases from NH<sub>3</sub> to BiH<sub>3</sub>.
  - (h) The shape of these hydrides is pyramidal. The formation is due to  $sp^3$  hybridization. The bond angle is never equal to ideal angle 109°28′. The actual angle in NH<sub>3</sub> is 106°5′.
  - Hydrogen bonding is present in NH<sub>3</sub>. No hydrogen bonding is present in other hydrides.
- 13. Except nitrogen, the rest of the elements of group 15 form two series of halides  $MCl_3$  and  $MCl_5$ . However, all form trihalides but one or more pentahalides are formed. Nitrogen does not form pentahalides due to absence of d-orbitals.
  - (a) All the trihalides are stable except NCl<sub>3</sub>, NBr<sub>3</sub> and NI<sub>3</sub>. The unstable nature is due to low polarity of N—X and a large difference in the size of N and Cl.
  - (b) The trihalides have distorted tetrahedral structure involving  $sp^3$  hybridization.
  - (c) The trihalides act as Lewis bases. This tendency decreases from N to Bi.
  - (d) Except NF<sub>3</sub> and PF<sub>3</sub>, all the trihalides are hydrolysed by water.
  - (e) Except N and Bi, other members form pentahalides especially fluorides.
  - (f) Pentahalides have a trigonal bipyramid shape  $(sp_s^3d)$  hybridization).
  - (g) Pentahalides decompose on heating into lower halides.
  - (h) Pentahalides are hydrolysed by water.
  - (i) X-ray studies have shown that solid PCl<sub>5</sub> is an ionic compound composed of [PCl<sub>4</sub>]<sup>+</sup>[PCl<sub>6</sub>]<sup>-</sup>. Solid PBr<sub>5</sub> exists as [PBr<sub>4</sub>]<sup>+</sup> Br<sup>-</sup>.
- 14. With the exception of nitrogen, all other elements of group 15 form sulphides. The sulphides of arsenic and antimony are soluble in yellow ammonium sulphide or ammonium sulphide and form thio-compounds.
- **15.** Nitrogen differs from the rest of the family members on account of following factors:
  - (a) small size of nitrogen atom.
  - (b) high value of electronegativity.
  - (c) absence of d-orbitals in the valency shell.
  - (d) tendency to form multiple bonds.

- 16. Scheele showed that air is a mixture of two gases: fire air (oxygen) and foul air (nitrogen). D.Rutherford named foul air as mephitic air (killer of life). Later on the element was found to be present in nitre and thus, the name nitrogen was proposed.
- 17. Nitrogen can be obtained either from air or from the nitrogen compounds. In the laboratory, it is obtained by heating a mixture of ammonium chloride and sodium nitrite (NH<sub>4</sub>NO<sub>2</sub>) or ammonium dichromate. Pure nitrogen is obtained by passing ammonia vapours on heated CuO. It is also formed by action of nitrous acid on urea.
- 18. Nitrogen is a colourless, odourless and tasteless gas. It is not poisonous but animals do not survive in its atmosphere due to absence of oxygen. It is non-combustible and does not help in combustion. It combines with oxygen, hydrogen, boron, silicon and certain metals under specific conditions. It combines with CaC<sub>2</sub> to form nitrolim (CaCN<sub>2</sub>+C) at 1000°C, which is used as a fertilizer.
- 19. Nitrogen forms three hydrides: (i) ammonia (NH<sub>3</sub>) (ii) hydrazine (NH<sub>2</sub>·NH<sub>2</sub>) and (iii) hydrazoic acid (N<sub>3</sub>H). Ammonia is obtained on a small scale by the action of caustic soda or lime on ammonium compounds, by reacting nitrides with water, by doing reduction of nitrates and nitrites with zinc and caustic soda, by heating ammonium compounds and by action of NaOH on urea.
- **20.** For drying of NH<sub>3</sub>, quicklime (CaO) is used. Other dehydrating agents like H<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> cannot be used as they react with NH<sub>3</sub>.
- 21. On large scale, ammonia is manufactured:(i) by Haber process (ii) by Bosch's process (iii) by cyanamide process or as a by-product during coal distillation.
- 22. NH<sub>3</sub> is lighter than air and is highly soluble in water due to hydrogen bonding. It can be easily liquefied at room temperature by application of pressure. Liquid NH<sub>3</sub> has a large heat of vaporisation. It is, therefore, used in ice plants. Ammonia is a Lewis base as it donates an electron pair. It forms ammonium salts with acids. It is oxidised to nitrogen. When chlorine in excess, an explosive substance NCl<sub>3</sub> is formed. Iodine flakes when rubbed with liquor ammonia form a dark brown precipitate of ammoniated nitrogen iodide (NH<sub>3</sub>NI<sub>3</sub>) which explodes readily on drying.
  - Aqueous ammonia (NH<sub>4</sub>OH) form many metal hydroxides. Some of them remain in solution in the form of complex compounds.
- 23. Alkaline solution of K<sub>2</sub>HgI<sub>4</sub> (Nessler's reagent) gives brown precipitate with NH<sub>3</sub> called iodide of Millon's base (H<sub>2</sub>NHgOHgI).
- 24. Ammonia is used for the manufacture of nitric acid, sodium bicarbonate and ammonium compounds. Ammonium sulphate, ammonium calcium nitrate, etc., are used as fertilizers. Ammonium nitrate is used in certain explosives. Ammonium hydroxide is used in laboratory. It is also used for the manufacture of urea and for making artificial silk. Liquid NH<sub>3</sub> is used in refrigeration.
- 25. Nitrogen forms five oxides: (i) N<sub>2</sub>O, nitrous oxide (laughing gas) (ii) NO, nitric oxide (iii) N<sub>2</sub>O<sub>3</sub>, nitrogen trioxide (iv) NO<sub>2</sub> or N<sub>2</sub>O<sub>4</sub>, nitrogen dioxide (v) N<sub>2</sub>O<sub>5</sub>, nitrogen pentoxide.

- (a) Except  $N_2O_5$ , all oxides of nitrogen are gases at room temperature.
- (b) N<sub>2</sub>O and NO are neutral oxides while N<sub>2</sub>O<sub>3</sub>, NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> are acidic oxides. The acidic nature increases as percentage of oxygen increases.
- (c) N<sub>2</sub>O is a colourless gas with pleasant odour and sweet taste. When inhaled in moderate quantity, it produces hysterical laughter, hence named as laughing gas. N<sub>2</sub>O is a linear and unsymmetrical molecule.

$$[: \stackrel{\stackrel{-}{N}}{=} \stackrel{+}{N} = \stackrel{\stackrel{-}{O}}{:} \longleftrightarrow : \stackrel{+}{N} = \stackrel{\stackrel{-}{N}}{\longrightarrow} \stackrel{\stackrel{-}{O}}{:}]$$

It is used as anaesthetic in dental or other minor surgical operations in form of a mixture of  $N_2O$  and  $O_2$ .

- (d) NO is a colourless gas, slightly heavier than air. It is paramagnetic indicating the presence of unpaired electron in the molecule (:N •••• O:).
  - In the liquid and solid states, it forms a loose dimer,  $N_2O_2$ .
- (e) N<sub>2</sub>O<sub>3</sub> condenses to a blue coloured liquid at -30°C. The liquid when warmed decomposes into NO and NO<sub>2</sub>. It is called nitrous anhydride as forms nitrous acid with water. It is represented as O=N-O-N=O.
- (f) NO<sub>2</sub> is a brown coloured gas with pungent odour. The liquid and solid is entirely N<sub>2</sub>O<sub>4</sub> (dimer) at low temperature. The molecule is V-shaped with O—N—O bond angle 132° and N—O bond length 1.19 Å. The molecule is an odd electron molecule.
- (g) N<sub>2</sub>O<sub>5</sub> is a white crystalline solid. It is formed by action of P<sub>2</sub>O<sub>5</sub> with conc. HNO<sub>3</sub>. It reacts with water and forms nitric acid. It is, thus, known as nitric anhydride. It exists as a symmetrical molecule in gaseous state, O<sub>2</sub>NONO<sub>2</sub>. X-rays studies reveal that solid N<sub>2</sub>O<sub>5</sub> is ionic in nature, i.e., nitronium nitrate NO<sub>2</sub><sup>+</sup>NO<sub>3</sub><sup>-</sup>.
- 26. Nitrous acid is unknown in free state but known only in solutions. It forms two series of organic derivatives, the nitrites (R—ONO) and nitro compounds (R—NO<sub>2</sub>). It is, thus, considered to be tautomeric mixture of two forms (HON=O and H—N—O).
- 27. HNO<sub>3</sub>, nitric acid was earlier called as *aqua fortis* (meaning strong water). It is a monobasic acid. It reacts with basic oxides, carbonates, bicarbonates and hydroxides forming corresponding salts. It usually acquires yellow colour, due to its decomposition by sunlight into NO<sub>2</sub>. The yellow colour can be removed by warming it to 60–80°C and bubbling dry air through it. It has extremely corrosive action on skin and causes painful sores.

It acts as a strong oxidising agent. Non-metals are converted into highest oxyacids by hot and conc. HNO<sub>3</sub>. NO<sub>2</sub> gas is evolved (S to H<sub>2</sub>SO<sub>4</sub>; P to H<sub>3</sub>PO<sub>4</sub>, C to H<sub>2</sub>CO<sub>3</sub>; I<sub>2</sub> to HIO<sub>3</sub>; As to H<sub>3</sub>AsO<sub>4</sub>; Sb to H<sub>3</sub>SbO<sub>4</sub> and Sn to H<sub>2</sub>SnO<sub>3</sub>). Most of the metals except noble metals are attacked by HNO<sub>3</sub>. It plays double role in action on metals, *i.e.*, it acts as an acid as well as an oxidising agent. Before the hydrogen is allowed to escape, nitric acid is reduced into number of products such

as NO<sub>2</sub>, NO, N<sub>2</sub>O, N<sub>2</sub> or NH<sub>3</sub>. It also oxidises a number of compounds.

Concentration of nitric acid	Metal	Main products
Very Dilute HNO <sub>3</sub>	Mg, Mn	H <sub>2</sub> + metal nitrate
very Email Title3	Fe, Zn, Sn	NH <sub>4</sub> NO <sub>3</sub> + metal nitrate
	Pb, Cu, Ag, Hg	NO + metal nitrate
Dilute HNO <sub>3</sub>	Fe, Zn	N <sub>2</sub> O + metal nitrate
	Zn, Fe, Pb, Cu, Ag	NO <sub>2</sub> + metal nitrate
Conc. HNO <sub>3</sub>	-Sn	NO <sub>2</sub> + H <sub>2</sub> SnO <sub>3</sub> Metastannic acid
Conc. HNO <sub>3</sub>	Fe, Co, Ni, Cr, Al	rendered passive

- **28.** Noble metals like gold, platinum, iridium, rhodium, etc., dissolve in aqua-regia (3 parts conc. HCl plus one part conc. HNO<sub>3</sub>). Aqua-regia forms nascent chlorine which attacks noble metals.
- **29.** The replacement of one or more hydrogen atoms of an organic compound by a nitro group (—NO<sub>2</sub>) is known as nitration. The nitration occurs in presence of conc. H<sub>2</sub>SO<sub>4</sub> with the formation of nitronium ion, NO<sub>2</sub><sup>+</sup>.

$$HNO_3 + 2H_2SO_4 \Longrightarrow NO_2^+ + 2HSO_4^- + H_3O_4^+$$

Proteins are attacked by HNO<sub>3</sub> forming a yellow nitro compound called **xanthoprotein**.

A number of organic compounds are oxidised. Sawdust catches fire when HNO<sub>3</sub> is poured over it. Turpentine oil bursts into flame when treated with fuming HNO<sub>3</sub>. Cane sugar is oxidised to oxalic acid.

- **30.** HNO<sub>3</sub> is used in the manufacture of explosives like T.N.T., picric acid, nitroglycerine, etc. It is also used in the manufacture of fertilizers, artificial silk, dyes, drugs, perfumes, sulphuric acid, nitrates, etc. It is a laboratory reagent used as a solvent for metals.
- **31.** The name phosphorus has been derived from the property of glowing in the dark.

(Greek word, phos = light and phero = I carry.)

Phosphorus is extracted either from phosphorite or bone ash by the application of either retort process (old process) or electrothermal process (modern process). In the modern process, phosphorite is mixed with carbon and silica. The mixture is introduced into the electric furnace and heated at 1400–1600°C. Vapours of phosphorus are condensed under water. It is further purified by melting under acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and is redistilled.

- **32.** Phosphorus exists in a number of allotropic forms. These are:
  - (a) yellow or white phosphorus
  - (b) red phosphorus
  - (c) scarlet phosphorus
  - (d) black phosphorus

The main allotropic forms are yellow and red.

The yellow form is the common variety. This form is chemically active. It is a transparent waxy solid and can be easily cut with knife. It has garlic odour and is poisonous in nature. Vapours are also injurious. Persons working with phosphorus develop a disease known as phossy jaw.

This form undergoes slow combustion in contact with air and glows in dark. This property is called chemiluminescence. It readily catches fire giving dense fumes of P<sub>2</sub>O<sub>5</sub> and therefore, kept in water.

When heated in inert atmosphere at 240°C, it changes into red variety. It is odourless and non-poisonous in nature. It does not show phosphorescence. It is not active in nature. It is regarded as a polymer consisting of P<sub>4</sub> tetrahedral chains.

- 33. Yellow phosphorus is used as a rat poison. Red phosphorus is used in match industry and for making of HBr and HI. Radioactive phosphorus (P<sup>32</sup>) is used in the treatment of leukemia and other blood disorders. It is used for making incendiary bombs and smoke screens.
- 34. Phosphine is prepared by boiling yellow phosphorus with a concentrated solution of sodium hydroxide in inert atmosphere. Besides PH<sub>3</sub>, small amounts of H<sub>2</sub> and P<sub>2</sub>H<sub>4</sub> are also formed. As soon as the bubbles of the gas come in contact with air, they catch fire forming rings of smoke known as vortex rings. This combustion is due to presence of P<sub>2</sub>H<sub>4</sub>. Pure phosphine can be obtained by using alcoholic potassium hydroxide in place of aqueous NaOH. It is a colourless gas, heavier than air, garlic like odour and poisonous in nature. Pure PH3 does not spontaneously inflame. It burns in air or oxygen at 150°C. The spontaneous inflammability at the time of preparation (due to presence of P<sub>2</sub>H<sub>4</sub>) is used in making Holme's signals. The phosphine is less basic and more reducing than NH<sub>3</sub>. The bond angle H—P—H is 93°.
- 35. Phosphorus forms three important oxides. These exist in dimeric forms.
  - (i) Phosphorus trioxide (P<sub>4</sub>O<sub>6</sub>)
  - (ii) Phosphorus tetroxide (P<sub>4</sub>O<sub>8</sub>)
  - (iii) Phosphorus pentoxide (P<sub>4</sub>O<sub>10</sub>)

In the molecule of P<sub>4</sub>O<sub>6</sub>, the phosphorus atoms lie at the tetrahedral position with each other and the 6 oxygen atoms are inserted between them. Each P is bonded covalently to three O-atoms and each oxygen atom is bonded to two phosphorus atoms.

The structures of P<sub>4</sub>O<sub>8</sub> and P<sub>4</sub>O<sub>10</sub> are similar to P<sub>4</sub>O<sub>6</sub> with a difference that in P<sub>4</sub>O<sub>8</sub> two alternate P-atoms are also linked with an additional oxygen atom each and in P<sub>4</sub>O<sub>10</sub> each phosphorus atom is linked with an additional oxygen atom by a coordinate linkage.



Structure of P<sub>4</sub>O<sub>6</sub>

P<sub>4</sub>O<sub>10</sub> is most effective drying or dehydrating agent.

**36.** Following are some important compounds:

(i) Scheele's green

CuHAsO<sub>3</sub>

(ii) Graham salt

 $(NaPO_3)_6$ 

(iii) Paris green

(CH3COO)2Cu-3Cu(AsO2)2

(iv) Pearl white

**BiOCl** 

(v) Nitrophosphate

 $Ca(H_2PO_2)_2 + 2Ca(NO_3)_2$ 

(vi) Superphosphate of lime Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>H<sub>2</sub>O + 2CaSO<sub>4</sub>·2H<sub>2</sub>O

(vii) Thomas slag

2Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·CaSiO<sub>3</sub>

(viii) Sindri fertilizer

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

(ix) Nangal fertilizer (CAN) Ca(NO<sub>3</sub>)<sub>2</sub>·NH<sub>4</sub>NO<sub>3</sub>

(x) Amatol

80% NH<sub>4</sub>NO<sub>3</sub> + 20% T.N.T.

(xi) Ammonal

NH<sub>4</sub>NO<sub>3</sub> + Al powder

(small quantity)

(xii) Swarts reagent

SbF<sub>3</sub>

(xiii) Tartaremetic (Potassium antimonyl tartarate)

- (xiv) Angeli's salt Na<sub>2</sub>N<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O 37. Arsenic trioxide is called white arsenic and is a poison. Traces
- of arsenic are detected by Marsh test. 38. Hydrazine is called diacid base and can form salts with one or two equivalents of an acid. Hydrazine (NH<sub>2</sub>·NH<sub>2</sub>) and its derivatives are used as rocket-fuels.

Hydrazoic acid (N<sub>3</sub>H) is a fairly strong acid, stronger than acetic acid but weaker than mineral acids. N<sub>3</sub>, azide is a pseudohalogen ion. Hydrazoic acid acts both as oxidising and a reducing agent.

- 39. Both NF<sub>3</sub> and NH<sub>3</sub> have pyramidal structures with bond angles 102° and 107° respectively. Their dipole moments are different-NF<sub>3</sub> (0.24 D) and NH<sub>3</sub> (1.48 D). The difference is due to the fact that while the dipole moment due to N-F bonds in NF<sub>3</sub> are in opposite direction to the direction of dipole moment of the lone pair on N-atom which partly cancel out, the dipole moments of N—H bonds in NH3 are in the same direction of the dipole moment of the lone pair on N which add up.
- 40. In case of phosphorus trihalides,  $PX_3$  (X = F, Cl, Br, I) the bond angle increases from PF<sub>3</sub> to PI<sub>3</sub>.
- 41. Hydroxylamine, NH2OH, is a hydroxy hydride of nitrogen. It is a derivative of ammonia. It is a weaker base than NH<sub>3</sub>. It behaves as a mild reducing agent as well as an oxidising
- 42. Some ammonium compounds decompose without evolving NH<sub>3</sub>.

$$\begin{array}{c} NH_4NO_2 \longrightarrow N_2 + 2H_2O \\ NH_4NO_3 \longrightarrow N_2O + 2H_2O \\ (NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O \end{array}$$

# -••• PRACTICE PROBLEMS -•••-

## ■ Subjective Type Questions

#### 1. Answer the following:

- (i) Why nitrogen is less reactive at room temperature?
- (ii) NF<sub>5</sub> is not known. Why?
- (iii) Why BiH<sub>3</sub> is strongest reducing agent?
- (iv) Which oxide of nitrogen becomes brown when released in air?
- (v) Name two neutral oxides of nitrogen.

#### 2. Answer the following:

- (i) Why does PCl<sub>3</sub> fume in air?
- (ii) Which element of group 15 is found in abundance in nature?
- (iii) In which is the bond angle higher, PH<sub>4</sub><sup>+</sup> ion or PH<sub>3</sub> molecule?
- (iv) Are all the five bonds in PCl<sub>5</sub> molecule equivalent?
- (v) Name three allotropic forms of phosphorus. Which is most reactive?
- (vi) What does the word cryogen mean?

#### 3. Give reason:

- (a) Why is ammonia highly soluble in water?
- (b) Nitrogen dioxide is paramagnetic in gaseous state.
- (c) Why does NH<sub>3</sub> act as a Lewis base?
- (d) Why conc. H<sub>2</sub>SO<sub>4</sub> cannot be used as dehydrating agent for NH<sub>3</sub>?
- (e) Ammonia has higher boiling point than phosphine.

#### 4. Explain briefly, why:

- (a) White phosphorus is more reactive than red phosphorus?
- (b) Hydrazine is unstable?
- (c) Trihalides of nitrogen cannot be oxidised to pentahalides?
- (d) NO is paramagnetic whereas NO<sup>+</sup> is diamagnetic?
- (e) Does H<sub>3</sub>PO<sub>3</sub> act as a reducing agent but H<sub>3</sub>PO<sub>4</sub> does not?
- **5.** Give the names and formulae of the compounds described below:
  - (i) A compound of N, H and O which on heating gives laughing gas.
  - (ii) A compound of N, H and O which on heating gives nitrogen gas.
  - (iii) A compound of Ca, P and O which is found in bones.
  - (iv) A compound of N and H which is used as refrigerant.
  - (v) A compound of N and H which behaves like an acid.
  - (vi) A compound of N and H which is used as a rocket fuel.
  - (vii) A compound of N, H, S and O which is used as a fertilizer.
  - (viii) A compound of N, H and O which is used for making oximes.
  - (ix) Two neutral oxides of nitrogen.
  - (x) The oxyacid of phosphorus is used for the preparation of HBr and HI from bromides and iodides respectively.
- 6. Describe the action of heat on the following compounds:
  - (i) Ammonium nitrate
  - (ii) Ammonium nitrite
  - (iii) Ammonium chloride

- (iv) A mixture of NaNO2 and NH4Cl
- (v) Ammonium dichromate
- (vi) Orthophosphoric acid
- (vii) Phosphorus acid
- (viii) Hypophosphorus acid
- (ix) Copper nitrate
- (x) Silver nitrate
- 7. Complete and balance the following reactions:
  - (i)  $KNO_3 + FeSO_4 + H_2SO_4(conc.) \longrightarrow ....$
  - (ii)  $Mg + HNO_3 \longrightarrow \dots$
  - (iii)  $Cu + HNO_3 \longrightarrow NO + \dots + \dots$
  - (iv)  $Pb(NO_3)_2 \xrightarrow{\text{Heat}} PbO + \dots + \dots$
  - (v)  $CuSO_4 + NH_4OH(excess) \longrightarrow .....$
  - (vi)  $NH_3(excess) + Cl_2 \longrightarrow \dots + \dots$
  - (vii)  $NH_3 + Cl_2(excess) \longrightarrow \dots$
  - (viii) AgCl + NH<sub>4</sub>OH  $\longrightarrow$  ......
  - (ix)  $Ag(NH_3)_2Cl + HNO_3 \longrightarrow \dots$
  - (x)  $Ca_3(PO_4)_2 + SiO_2 + C \xrightarrow{Heat} CaSiO_3 + CO + \dots$
  - (xi)  $CaCN_2 + H_2O(steam) \longrightarrow CaCO_3 + \dots$
  - (xii)  $Ca_3(PO_4)_2 + H_3PO_4 \longrightarrow \dots$
  - (xiii)  $NH_3 + NaOCl \longrightarrow ..... + NaCl + H_2O$  [I.I.T. 1993]
  - (xiv)  $P_4O_{10} + PCl_5 \longrightarrow \dots$  [I.I.T. 1998]

#### 8. What happens when?

- (i) A mixture of air and ammonia is passed over heated platinum gauze. [M.L.N.R. 1990]
- (ii) Gold is treated with aqua-regia.
- [LLT. 1997]
- (iii) Water is added to calcium phosphide.
- (iv) Calcium phosphate is heated with a mixture of sand and carbon.
- (v) Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide.
- (vi) Zinc is treated with very very dilute nitric acid.
- (vii) Phosphine is treated with an acidified CuSO<sub>4</sub> solution. [M.L.N.R. 1990]
- (viii) Iodine reacts with concentrated nitric acid.

[M.L.N.R. 1992]

- (ix) Orthophosphoric acid is heated with nitric acid and ammonium molybdate.
- (x) Disodium hydrogen phosphate is added to ammonical solution of magnesium sulphate.
- (xi) Magnesium is burnt in air and the product is treated with water.
- (xii) Phosphine is passed through AgNO3 solution.
- (xiii) Phosphoric acid reacts with Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F. [LI.T. 1998]

#### 9. How will you prepare?

- (i) Ammonia from calcium carbide.
- (ii) Nitrogen from ammonium chloride.
- (iii) Phosphine from phosphorus.

- (iv) Phosphorus from bone ash.
- (v) Nitrous oxide from dilute nitric acid.
- (vi) Nitrogen dioxide from concentrated nitric acid.
- (vii) Ammonium nitrate from nitric acid.
- (viii) Yellow phosphorus from orthophosphoric acid.
- (ix) Metaphosphoric acid from orthophosphoric acid.
- (x) Hydrogen from nitric acid.

#### 10. Answer the following:

- (i) How many unpaired electrons are present in the valency shell of VA group elements?
- (ii) How many covalent bonds nitrogen can form?
- (iii) What are the minimum and maximum oxidation states of nitrogen?
- (iv) Which oxyacid of nitrogen behaves both as an oxidising and a reducing agent?
- (v) Why NH<sub>3</sub> exists as liquid whereas other hydrides of the same group exist as gases?
- (vi) Which oxide of nitrogen is paramagnetic and coloured?
- (vii) What are the possible oxidation states for nitrogen? Give an example of each.
- (viii) What is the basicity of hypophosphorus acid?
- (ix) Which allotropic form of phosphorus is more active?
- (x) What is the shape of phosphorus molecule?

### 11. Arrange the following as directed:

- (i) N, P, As, Sb and Bi (increasing order of stability of +5 oxidation state)
- (ii) NCl<sub>3</sub>, PCl<sub>3</sub>, AsCl<sub>3</sub>, SbCl<sub>3</sub> and BiCl<sub>3</sub> (order of ease of hydrolysis)
- (iii) NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub> and SbH<sub>3</sub> (increasing order of basic nature)
- (iv) NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub> and BiH<sub>3</sub> (increasing order of stability)

#### 12. How will you obtain?

- (a)  $N_2$  from a mixture of  $N_2$  and CO.
- (b) NH<sub>4</sub>Cl from a mixture of NH<sub>4</sub>Cl and KCl.
- (c) Nitrogen from a mixture of N<sub>2</sub> and O<sub>2</sub>.
- (d) NH<sub>3</sub> from a mixture of N<sub>2</sub> and NH<sub>3</sub>.
- (e) PH<sub>3</sub> from a mixture of PH<sub>3</sub> and NH<sub>3</sub>.
- (f)  $N_2$  from a mixture of  $N_2$  and  $CO_2$ .

#### 13. Write down the formulae of the following:

- (i) Sal ammoniac
- (ii) Laughing gas
- (iii) Superphosphate of lime
- (iv) Triple superphosphate
- (v) Nitrophosphate
- (vi) Leuna saltpetre
- (vii) Nitrochalk
- (viii) Sindri fertilizer
- (ix) CAN
- (x) Nitrolim
- 14. (a) Write the two resonance structures of N<sub>2</sub>O that satisfy the octet rule. [1.1.T. 1990; M.L.N.R. 1993]
  - (b) Give the structural formulae of phosphorus acid  $(H_3PO_3)$  and pyrophosphoric acid  $(H_4P_2O_7)$ .

- (c) Draw the structure of P<sub>4</sub>O<sub>10</sub> and identify the number of single and double P—O bonds. [I.I.T. 1996]
- (d) Draw the structure of P<sub>4</sub>O<sub>6</sub> and identify the number of single P—O bonds.
- (e) Write down the Lewis electron dot formula of the following:

NO, N<sub>2</sub>O<sub>5</sub>, HNO<sub>2</sub>, HNO<sub>3</sub>, PH<sub>4</sub>I, H<sub>3</sub>PO<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>.

(f) Write down the shapes of the following:

- 15. Write short notes on the following:
  - (a) Nitrogen fertilizers(b) Phosphorus fertilizer
  - (b) Phosphorus fertilizers
  - (c) Mixed fertilizers
  - (d) Action of nitric acid on metals
  - (e) Action of nitric acid on non-metals
  - (f) Nitrogen cycle
  - (g) Nitrogen fixation
  - (h) Oxidation states of nitrogen
  - (i) Oxides of nitrogen
  - (i) Nitrates
  - (k) Holme's signal
  - (l) Uses of nitric acid
  - (m) Passivity
- **16.** Describe the principle of manufacture with conditions of the following compounds:
  - (i) Ammonia by Haber process.
  - (ii) Nitric acid by Ostwald's process.
  - (iii) White phosphorus from bone ash by electrothermic method.
  - (iv) Ammonium sulphate from gypsum. [I.I.T. 1990]
  - (v) Superphosphate of lime.
  - (vi) Nitrolim.
  - (vii) Urea.
- 17. Explain the following with relevent reason:
  - (i) Nitric acid turns yellow in sunlight.

[Ans. HNO<sub>3</sub> decomposes to form yellow N<sub>2</sub>O<sub>4</sub> in sunlight.

$$4HNO_3 \xrightarrow{Sunlight} 2H_2O + 2N_2O_4 + O_2$$

(ii) Why nitrate and nitrite cannot be distinguished by the action of conc. H<sub>2</sub>SO<sub>4</sub>?

[Ans. Because both liberate brown fumes of NO<sub>2</sub> on heating with conc. H<sub>2</sub>SO<sub>4</sub>.]

(iii) Why NO<sub>2</sub> cannot be dried by means of NaOH solution?

[Ans. NO2 is an acidic gas. It is absorbed in NaOH.]

(iv) On heating Pb(NO<sub>3</sub>)<sub>2</sub> produces a pale yellow gas which on strong heating produces a brown gas.

[Ans. Lead nitrate first produces N<sub>2</sub>O<sub>4</sub> which is pale yellow. On further heating, it decomposes into nitrogen dioxide (brown in colour).

$$\begin{array}{c} \text{Pb}(\text{NO}_3)_2 \xrightarrow{\text{Heating}} & \text{N}_2\text{O}_4 \xrightarrow{\text{Heating}} & \text{NO}_2 \\ & \text{A pale} & & \text{A brown} \\ & & \text{yellow gas} & & \text{gas} \end{array}$$

(v) Water has the highest boiling point among NH<sub>3</sub>, PH<sub>3</sub>, HCl and H<sub>2</sub>O.

[Ans. Maximum hydrogen bonding is present in water as oxygen is the most electronegative among N, P, Cl and O.]

(vi) Nitric acid mostly forms oxides of nitrogen on reacting with metals while other acids react with metals to evolve hydrogen.

[Ans. In addition to being an acid, nitric acid is a strong oxidising agent. Before hydrogen is evolved, it reduces nitric acid into nitrogen oxides.]

(vii) Phosphine is prepared in an inert atmosphere of carbon dioxide or hydrogen.

[Ans. Phosphine, being highly inflammable, burns in air. It is therefore prepared in inert atmosphere.]

(viii) Red phosphorus is used for making matches.

[Ans. Red phosphorus is non-poisonous and has a high ignition point.]

(ix) Phosphorus pentoxide is used in the preparation of N<sub>2</sub>O<sub>5</sub>.

[Ans. P<sub>4</sub>O<sub>10</sub> is a strong dehydrating agent. It removes water molecules from nitric acid to form N<sub>2</sub>O<sub>5</sub>.

$$P_4O_{10} + 12HNO_3 \longrightarrow 4H_3PO_4 + 6N_2O_5$$
  
or  $P_4O_{10} + 4HNO_3 \longrightarrow 4HPO_3 + 2N_2O_5$ 

(x) Ammonia is used for refrigeration.

[Ans. Ammonia has high heat of vaporisation.]

(xi) The electronegativity of both nitrogen and chlorine is the same. But nitrogen is inert at room temperature whereas chlorine is highly reactive.

[Ans. Nitrogen molecule consists a strong triple bond whereas a chlorine molecule has only a single bond.]

(xii) Ammonia acts as a ligand.

[Ans. Due to the presence of a lone pair of electrons on nitrogen which it can donate to acceptor (a metal ion) and thus acts as a ligand.]

(xiii) Burning magnesium continues to burn in nitric oxide while burning sulphur is extinguished.

[Ans. The reaction between Mg and O<sub>2</sub> is highly exothermic, *i.e.*, the heat evolved is enough to decompose NO into N<sub>2</sub> and O<sub>2</sub> while the heat evolved during burning of sulphur is not sufficient to break NO.]

(xiv) NF<sub>3</sub> is not hydrolysed but NCl<sub>3</sub> is readily hydrolysed.
[Ans. Neither nitrogen nor fluorine possess vacant d-orbitals to form extra bond with lone pair of electrons on oxygen of water molecule. However, NCl<sub>3</sub> has vacant d-orbitals on chlorine atom.

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HClO$$

(xv) Aluminium containers can be used for strong concentrated HNO<sub>3</sub>.

[Ans. Aluminium is rendered passive by conc. HNO<sub>3</sub> due to formation of a fine film of its oxide on its surface. This film does not allow the dissolution of aluminium metal in acid and thus Al-containers can be used to store conc. HNO<sub>3</sub>.]

(xvi) Pure PH<sub>3</sub> does not burn in air but impure sample of PH<sub>3</sub> burns in air.

[Ans. P<sub>2</sub>H<sub>4</sub>, the liquid hydride is always present in impure phosphine. It catches fire as soon as it comes in contact with air.]

(xvii) Phosphorus does not form phosphorus penta-iodide. [Ans. Due to large size of iodine, the effective overlapping between the orbitals of P and I is not possible to form covalent bonds.]

(xviii) Phosphorus acid is a dibasic acid.

[Ans. Phosphorus acid molecule, H<sub>3</sub>PO<sub>3</sub>, possesses two hydroxyl groups, *i.e.*, two replaceable hydrogen atoms.



(xix) Urea is a better nitrogenous fertilizer than ammonium sulphate.

[Ans. Urea on hydrolysis gives NH<sub>3</sub> and CO<sub>2</sub>. NH<sub>3</sub> is assimilated by plants and CO<sub>2</sub> goes to atmosphere, *i.e.*, no residue is left in soil. Ammonium sulphate on hydrolysis gives NH<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. NH<sub>3</sub> is assimilated while H<sub>2</sub>SO<sub>4</sub> is retained in soil making it acidic.]

(xx)  $(SiH_3)_3N$  is a weaker base than  $(CH_3)_3N$ . [I.I.T. 1995] [Ans. In  $(SiH_3)_3N$ , the lone pair of electrons on nitrogen is used up in  $p\pi$ - $d\pi$  back bonding. Such a  $p\pi$ - $d\pi$  bonding is not possible in  $(CH_3)_3N$  due to absence of d-orbitals in carbon. This accounts for more basic nature of  $(CH_3)_3N$  than  $(SiH_3)_3N$ .]

(xxi) Mg<sub>3</sub>N<sub>2</sub> when reacted with water gives off NH<sub>3</sub> but HCl is not obtained from MgCl<sub>2</sub> on reaction with water at room temperature. [L.I.T. 1995]

[Ans. MgCl<sub>2</sub> is a salt of a strong acid and a strong base so its hydrolysis is not possible whereas Mg<sub>3</sub>N<sub>2</sub> is a salt of a strong base, Mg(OH)<sub>2</sub>, and a weak acid, NH<sub>3</sub>, so it gets hydrolysed to give NH<sub>3</sub>.]

(xxii) Aqua-regia dissolves gold.

[Ans. Aqua-regia is a mixture of conc. HNO<sub>3</sub> and conc. HCl. Both react to give nascent chlorine which attacks gold and forms gold chloride which dissolves.]

(xxiii) Calcium cyanamide is used as a fertilizer.

[Ans. In soil, it is converted into urea which then decomposes into ammonia. This is assimilated by plants.

$$\begin{array}{c} \text{CaCN}_2 + \text{H}_2\text{O} + \text{CO}_2 & \longrightarrow \text{CN} \cdot \text{NH}_2 + \text{CaCO}_3 \\ & \text{Cyanamide} \\ \\ \text{CN} \cdot \text{NH}_2 + \text{H}_2\text{O} & \longrightarrow \text{NH}_2\text{CONH}_2 \end{array}$$

$$NH_2CONH_2 + H_2O \longrightarrow 2NH_3 + CO_2$$
 ]

(xxiv) Nitric oxide turns brown in air.

[Ans. Nitric oxide directly reacts with oxygen of the air forming brown fumes of  $NO_2$ .

$$2NO + O_2 \longrightarrow 2NO_2$$

(xxv) Copper dissolves in HNO3 but not in HCl.

[Ans. HNO<sub>3</sub> is an oxidising agent which converts copper into CuO which dissolves in HNO<sub>3</sub> in the form of copper nitrate.]

- 18. (i) An inorganic iodide (A) on heating with a solution of KOH gives a gas (B) and the solution of a compound (C).
  - (ii) The gas (B) on ignition in air gives a compound (D) and water.
  - (iii) Copper sulphate is reduced to the metal on passing (B) through the solution.
  - (iv) A precipitate of the compound (E) is formed on reaction of (C) with copper sulphate solution.

Identify (A) to (E) and give chemical equations for reactions at steps (i) to (iv). [Roorkee 1994]

[Hint: Gas (B) on ignition gives water, therefore, hydrogen is present in the gas.

An inorganic iodide with alkali (KOH) gives a gas (B), a hydrogen compound, so (A) may be NH<sub>4</sub>I or PH<sub>4</sub>I. As NH<sub>3</sub> does not reduce CuSO<sub>4</sub>, therefore, the compound (A) is PH<sub>4</sub>I.

(i) 
$$PH_4I + KOH \longrightarrow PH_3 + KI + H_2O$$
  
 $(A)$   $(B)$   $(C)$   
(ii)  $4PH_3 + 8O_2 \longrightarrow P_4O_{10} + 6H_2O$   
 $P_4O_{10} + 2H_2O \longrightarrow 4HPO_3$   
 $(D)$   
Metaphosphoric

(iv) 
$$2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$$
]  
(C) (E)

19. An orange solid (A) on heating gave a green residue (B), a colourless gas (C) and water vapour. The dry gas (C) on passing over heated magnesium gave a white solid (D). (D) on reaction with water gave a gas (E) which formed dense white fumes with HCl. Identify (A) to (E) and give the reactions.

[I.I.T. 1992]

[Hint: Formation of dense white fumes with HCl indicates that the gas (E) is NH<sub>3</sub>.

Ammonia is formed by hydrolysis of solid (D). Thus, (D) should be  $Mg_3N_2$ .

Formation of (D) indicates that gas (C) is  $N_2$ . Thus, (A) is ammonium dichromate.

$$\begin{array}{cccc} (NH_4)_2Cr_2O_7 & \longrightarrow & N_2 + Cr_2O_3 + 4H_2O \\ \text{Orange (A)} & (C) & \text{Green (B)} \end{array}$$
 
$$3Mg + N_2 & \longrightarrow & Mg_3N_2 \ (D)$$
 
$$Mg_3N_2 + 6H_2O & \longrightarrow & 3Mg(OH)_2 + 2NH_3 \\ NH_3 + HCl & \longrightarrow & NH_4Cl \ ]$$
 Dense white fumes

20. Gradual addition of KI solution to Bi(NO<sub>3</sub>)<sub>3</sub> solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions. [LI.T. 1996]

[Hint: Bi(NO<sub>3</sub>)<sub>3</sub> undergoes hydrolysis forming nitric acid. Nitric acid liberates iodine from KI which dissolves in excess of KI giving clear yellow solution.

$$\begin{array}{c} \text{Bi}(\text{NO}_3)_3 \ + \ \text{H}_2\text{O} \ \longrightarrow \ [\text{Bi}(\text{OH})(\text{NO}_3)_2] \ + \ \text{HNO}_3 \\ 2\text{HNO}_3 \ \longrightarrow \ \text{H}_2\text{O} \ + \ 2\text{NO}_2 \ + \ \text{O} \\ 2\text{KI} \ + \ 2\text{HNO}_3 \ + \ \text{O} \ \longrightarrow \ 2\text{KNO}_3 \ + \ \text{H}_2\text{O} \ + \ \text{I}_2 \\ \text{(Dark brown ppt.)} \\ \text{I}_2 \ + \ \text{KI} \ \longrightarrow \ \ \ \ \ \text{KI}_3 \ ] \\ \text{Yellow solution} \end{array}$$

21. A colourless solid (A) liberates a brown gas (B) on acidification, a colourless alkaline gas (C) on treatment with NaOH and a colourless non-reactive gas (D) on heating. If heating of the solid (A) is continued, it completely disappears. Identify (A) to (D).

[Ans. 
$$(A) = NH_4NO_2$$
;  $(B) = NO_2$ ;  $(C) = NH_3$ ;  $(D) = N_2$ ]

22. A compound (A) on heating with an excess of caustic soda solution liberates a gas (B) which gives white fumes on exposure to HCl. Heating is continued to expel the gas completely. The resultant alkaline solution again liberates the same gas (B) with zinc powder. However, the compound (A) when heated alone, does not give nitrogen. Identify (A) and (B).

[Ans. 
$$(A) = NH_4NO_3$$
;  $(B) = NH_3$ ]

- 23. An inorganic compound (A) when heated decomposes completely to give only two gases (B) and (C). (B) is a neutral gas, fairly soluble in water and itself decomposes on heating to two different gases (D) and (E).
  - (A) when warmed with NaOH gives another gas (F) which turns mercurous nitrate paper black. After sometime the gas (F) ceases to evolve, however its supply is restored by treating residual solution with aluminium powder. Identify (A) to (F) and give necessary equations.

$$\begin{array}{c} \text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}; \\ 2\text{N}_2\text{O} \xrightarrow{\text{Heat}} 2\text{N}_2 + \text{O}_2 \\ \\ \text{NH}_4\text{NO}_3 + \text{NaOH} \longrightarrow \text{NaNO}_3 + \text{NH}_3 + \text{H}_2\text{O} \\ \\ \text{Al} + \text{NaOH} + \text{H}_2\text{O} \longrightarrow \text{NaAlO}_2 + 3\text{H} \\ \\ \text{NaNO}_3 + 8\text{H} \longrightarrow \text{NaOH} + \text{NH}_3 + 2\text{H}_2\text{O} \\ \end{array}$$

24. In the following reaction,

$$A + 2B + H_2O \longrightarrow C + 2D$$
  
 $(A = \text{HNO}_2, B = \text{H}_2\text{SO}_3, C = \text{NH}_2\text{OH}). \text{ Identify } D.$   
[LI.T. 1999]  
[Ans.  $\text{HNO}_2 + 2\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{NH}_2\text{OH} + 2\text{H}_2\text{SO}_4]$   
(A) (B) (C) (D)

- 25. (i) Sodium salt of an acid (A) is formed on boiling white phosphorus with NaOH solution.
  - (ii) On passing chlorine through phosphorus kept fused under water, another acid (B) is formed which on strong heating gives metaphosphorus acid.
  - (iii) Phosphorus on treatment with conc. HNO<sub>3</sub> gives an acid (C) which is also formed by the action of dilute H<sub>2</sub>SO<sub>4</sub> on powdered phosphorite rock.
  - (iv) (A) on treatment with a solution of HgCl<sub>2</sub> first gives a white precipitate of compound (D) and then a grey precipitate of (E).

Identify (A) to (E) and write balanced equations for the reactions at steps (i) to (iv). [Roorkee 2001] [Hint: (i)  $P_4 + 3NaOH + 3H_2O \longrightarrow$ 3NaH<sub>2</sub>PO<sub>2</sub> + PH<sub>3</sub> Sodium hypophosphite

Thus, acid (A) is H<sub>3</sub>PO<sub>2</sub>, i.e., hypophosphorus acid.

(ii) 
$$2P + 3Cl_2 \longrightarrow 2PCl_3$$
  
 $2PCl_3 + 6H_2O \longrightarrow 2H_3PO_3 + 6HCl_3$ 

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2H_3PO_4 + 3CaSO_4$$
  
(Phosphorite rock)

(iv) 
$$H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$$
  
 $2HgCl_2 + 2H \longrightarrow Hg_2Cl_2 + 2HCl$   
(D)  
White ppt.

## Matching Type Questions

#### Match the following:

- [A] (a) Mephitic air
  - (b) Laughing gas

  - (c) Anhydride of HNO<sub>3</sub>
  - (d) Anhydride of HNO<sub>2</sub> (e) Anhydride of HPO<sub>3</sub>
  - (f) Dibasic acid
  - (g) Tribasic acid
  - (h) Acid hydride of nitrogen (viii) Nitrous oxide
  - Basic hydride of nitrogen
  - (j) Brown coloured gas
- [B] (a) CAN
  - (b) NPK
  - (c) Ammonium sulphate
  - (d) Nitrolim
  - (e) Ammonium nitrate
  - Salammoniac
  - (g) Explosive mixture
  - (h) Haber process
  - Ostwald's process (i)
  - Poisonous oxide
  - (k) Leuna saltpetre
  - Nitrochalk

6.

(v)

- (i) Phosphorus acid
- (ii) Hydrazoic acid
- (iii) Orthophosphoric acid
- (iv) Ammonia
- (v) Nitrogen dioxide
- (vi) Nitrogen pentoxide
- (vii) Phosphorus pentoxide
- (ix) Nitrogen
- (x) Nitrogen trioxide
- (i) Freezing salt
- (ii) Manufacture of NH3
- (iii) NH<sub>4</sub>NO<sub>3</sub>+CaCO<sub>3</sub>
- (iv) Arsenious oxide
- (v) Manufacture of HNO<sub>3</sub>
- (vi)  $NH_4NO_3 + (NH_4)_2SO_4$
- (vii) Nangal fertilizer
- (viii) Sindri fertilizer
- (ix) Calcium cyanamide
- (x) Ammonium chloride
- (xi) Mixed fertilizer
- (xii) Amatol

## Answers

#### **Answers**: Subjective Type Questions

- (i) The dissociation energy of nitrogen molecule is very high i.e., 941.4 kJ mol<sup>-1</sup>.
  - (ii) Nitrogen cannot extend its valency from 3 to 5 due to absence of d-orbitals.
  - (iii) BiH3 is least stable as Bi is bigger in size in comparison to the size of hydrogen.
  - (iv) Nitric oxide,  $2NO + O_2 \longrightarrow 2NO_2$ Colourless
  - (v) Nitrous oxide, N2O and nitric oxide, NO
- 2. (i) PCl<sub>3</sub> combines with moisture of air and undergoes hydrolysis giving fumes of HCl.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

- (ii) Phosphorus
- (iii) PH<sub>4</sub> ion
- (iv) No, Two axial P-Cl bonds are less stable than three equatorial P-Cl bonds. This is observed when PCl<sub>5</sub> is heated.

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

- (v) White or yellow, red and black. White phosphorus is most reactive.
- (vi) Freeze
- (a) Due to hydrogen bonding.
  - (b) Due to the presence of odd electron on nitrogen atom.
  - (c) Due to the presence of lone pair of electrons on nitrogen atom which can be donated.
  - (d) NH<sub>3</sub> combines with H<sub>2</sub>SO<sub>4</sub> and forms ammonium sulphate.
  - (e) Hydrogen bonding in NH3 makes it as an associated molecule.
- 4. (a) White phosphorus is more reactive due to higher angular strain in its molecule.

- (b) In hydrazine, there is N—N single bond with lone pair of electrons on each atom. Due to small size of nitrogen, there is considerable repulsion between these non-bonding electrons.
- (c) Because of non-availability of d-orbitals, nitrogen can not accommodate more than 8 electrons in its valence shell and therefore, its trihalides cannot be oxidised to pentahalides.
- (d) Nitric oxide is paramagnetic because of the presence of odd electron. When this electron is lost, NO<sup>+</sup> is formed which is diamagnetic.
- (e) H<sub>3</sub>PO<sub>3</sub> contains one P—H bond and acts as a reducing agent. H<sub>3</sub>PO<sub>4</sub> does not contain P—H bond.
- 5. (i) NH<sub>4</sub>NO<sub>3</sub> (ammonium nitrate); (ii) NH<sub>4</sub>NO<sub>2</sub> (ammonium nitrite); (iii) Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (calcium phosphate); (iv) NH<sub>2</sub> (ammonia); (v) N<sub>3</sub>H (hydrazoic acid); (vi) N<sub>2</sub>H<sub>4</sub> (hydrazine); (vii) (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (ammonium sulphate); (viii) NH2OH (hydroxylamine); (ix) N2O and NO; (x) H<sub>3</sub>PO<sub>4</sub> (orthophosphoric acid);

(i) 
$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

(ii) 
$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

(iii) 
$$NH_4C1 \rightleftharpoons NH_3 + HC1$$

(iv) 
$$\begin{aligned} \text{NaNO}_2 + \text{NH}_4\text{Cl} &\longrightarrow \text{NH}_4\text{NO}_2 + \text{NaCl} \\ \text{NH}_4\text{NO}_2 &\longrightarrow \text{N}_2 + 2\text{H}_2\text{O} \\ \hline \\ \text{NaNO}_2 + \text{NH}_4\text{Cl} &\longrightarrow \text{N}_2 + \text{NaCl} + 2\text{H}_2\text{O} \end{aligned}$$

 $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$ 

(vi) 
$$2H_3PO_4 \xrightarrow{250^{\circ}C} H_4P_2O_7 + H_2O$$
  
 $H_3PO_4 \xrightarrow{600^{\circ}C} HPO_3 + H_2O$ 

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4H_3PO_4 \xrightarrow{\text{Red hot}} P_4O_{10} + 6H_2O
                                4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3
       (vii)
      (viii)
                                2H_3PO_2 \longrightarrow H_3PO_4 + PH_3
                            2Cu(NO_3)_2 \longrightarrow 2CuO + 2NO_2 + O_2
        (ix)
                               2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2
         (x)
 7.
         (i)
                    2KNO_3 + H_2SO_4 \longrightarrow 2HNO_3 + K_2SO_4
                                 2HNO_3 \longrightarrow 2NO + H_2O + 3O
              [2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 3
                         [FeSO_4 + NO \longrightarrow FeSO_4 \cdot NO] \times 2
     2KNO_3 + 8FeSO_4 + 4H_2SO_4 \longrightarrow
                               3Fe_2(SO_4)_3 + 2FeSO_4 NO + K_2SO_4 + 4H_2O
                         Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2
         (ii)
                                 2HNO_3 \longrightarrow H_2O + 2NO + 3O
        (iii)
                 3Cu + 3O + 6HNO_3 \longrightarrow 3Cu(NO_3)_2 + 3H_2O
                        3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O
                             2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2
        (iv)
         (v)
                  CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2 + (NH_4)_2SO_4
Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \longrightarrow Cu(NH_3)_4SO_4 + 4H_2O
        (vi)
                          2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl
                         6NH_3 + 6HC1 \longrightarrow 6NH_4C1
                          8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2
                          (Excess)
                            NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl
        (vii)
                                    (Excess)
       (viii)
                       AgCl + NH<sub>4</sub>OH - → AgOH + NH<sub>4</sub>Cl
        AgOH + NH_4Cl + NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O
                     AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O
         (ix) Ag(NH_3)_2Cl + 2HNO_3 \longrightarrow AgCl + 2NH_4NO_3
                2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}
                          P_4O_{10} + 10C \longrightarrow 10CO + P_4
        2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow 6CaSiO_3 + 10CO + P_4
                        CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3
        (xii) Ca_3(PO_4)_2 + 4H_3PO_4 \longrightarrow 3Ca(H_2PO_4)_2
        (xiii)
                      2NH_3 + 3NaOC1 \longrightarrow N_2 + 3NaC1 + 3H_2O
                         NH<sub>3</sub> + NaOCl Glue. → NH<sub>2</sub>Cl + NaOH
           or
                         NH<sub>3</sub> + NH<sub>2</sub>Cl ---- NH<sub>2</sub>NH<sub>2</sub> + HCl
                          NaOH + HCl \longrightarrow NaCl + H_2O
                        2NH<sub>3</sub> + NaOCl \longrightarrow NH<sub>2</sub>·NH<sub>2</sub> + NaCl + H<sub>2</sub>O
                         P_4O_{10} + 6PCl_5 \longrightarrow 10POCl_3
        (xiv)
                           4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O
           (i)
                        [HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2Cl] \times 3
           (ii)
                               [Au + 3Cl \longrightarrow AuCl_3] \times 2
                          [AuCl_3 + HCl \longrightarrow HAuCl_4] \times 2
             2Au + 3HNO_3 + 11HCl \longrightarrow 2HAuCl_4 + 3NOCl + 6H_2O
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Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3
       (iii)
                2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}
       (iv)
                         P_4O_{10} + 10C \longrightarrow P_4 + 10CO
       2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow P_4 + 10CO + 6CaSiO_3
                               [2HNO_3 \longrightarrow NO + NO_2 + H_2O + 2O] \times 5
        (v)
                              P_4 + 100 \longrightarrow P_4O_{10}
                       P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4
              P_4 + 10HNO_3 + H_2O \longrightarrow 4H_3PO_4 + 5NO + 5NO_2
       (vi)
                        [Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4
                          HNO_3 + 8H \longrightarrow NH_3 + 3H_2O
                        HNO_3 + NH_3 \longrightarrow NH_4NO_3
                      4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O
       (vii)
                     3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4
                                [2HNO_3 \longrightarrow H_2O + 2NO_2 + O] \times 5
      (viii)
                                I_2 + 5O \longrightarrow I_2O_5
                           I_2O_5 + H_2O \longrightarrow 2HIO_3
                         I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O
        (ix) H_3PO_4 + 21HNO_3 + 12(NH_4)_2MoO_4 \longrightarrow
                              (NH_4)_3PO_4\cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O
         (x) Na_2HPO_4 + MgSO_4 + NH_4OH \longrightarrow
                                                 MgNH_4PO_4 + Na_2SO_4 + H_2O
        (xi) 3Mg + N_2 \longrightarrow Mg_3N_2 \xrightarrow{3H_2O} 3MgO + 2NH_3
       (xii)
                      3AgNO_3 + PH_3 \longrightarrow Ag_3P + 3HNO_3
       (xiii) Ca_5(PO_4)_3F + 7H_3PO_4 + 5H_2O \longrightarrow 5Ca(H_2PO_4)_2 \cdot H_2O + HF
                    CaC_2 \xrightarrow{N_2} CaCN_2 \xrightarrow{H_2O} NH_3
         (ii) NH_4Cl + NaNO_2 \longrightarrow NH_4NO_2 \longrightarrow N_2
                         P_4 + Ba(OH)_2 \xrightarrow{Heat} PH_3
        (iv) Bone Ash + Conc. H_2SO_4 \xrightarrow{Digested} H_3PO_4 -
                                                            Syrupy mass
                                                                   HPO<sub>3</sub> Heat
         (v)
                 Zn + HNO_3(Dilute) \longrightarrow N_2O
        (vi)
                  Cu + HNO_3(Conc.) \longrightarrow NO_2
       (vii) By passing NH3 through 60% HNO3.
                         NH_3 + HNO_3 \longrightarrow NH_4NO_3
                                  H_3PO_4 \xrightarrow{Heat} HPO_3 \xrightarrow{Coke} P_4
       (viii)
                                H<sub>3</sub>PO<sub>4</sub> Heat HPO<sub>3</sub> HPO<sub>3</sub>
         (ix)
         (x)
                     Mg + HNO_3(2\%) \longrightarrow Hvdrogen.
10. (i) Three; (ii) Four—3 covalent and one coordinate; (iii) -3 and +5;
       (iv) Nitrous acid; (v) Due to intermolecular hydrogen bonding in
       NH<sub>3</sub>; (vi) NO<sub>2</sub>; (vii) -3, -2, -1, -\frac{1}{3}, 0, +1, +2, +3, +4, +5 NH<sub>3</sub>
       (-3), NH_2NH_2 (-2), NH_2OH (-1), N_3H (-\frac{1}{2}), N_2 (0), N_2O (+1),
       NO (+2), N<sub>2</sub>O<sub>3</sub> (+3), N<sub>2</sub>O<sub>4</sub> (+4), N<sub>2</sub>O<sub>5</sub> (+5); (viii) one; (ix) yellow
       or white phosphorus; (x) tetrahedral.
          (i) Bi < Sb < As < P < N
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(ii)  $NCl_3 < PCl_3 < AsCl_3 < SbCl_3 < BiCl_3$ 

9.

11.

- (iii)  $SbH_3 < AsH_3 < PH_3 < NH_3$
- (iv)  $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$
- 12. (i) By bubbling through ammonical cuprous chloride in which CO is absorbed but not  $N_2$ .
  - (ii) By sublimation, NH<sub>4</sub>Cl sublimes leaving KCl as residue.
  - (iii) By bubbling through alkaline solution of pyrogallol in which oxygen is absorbed but not N<sub>2</sub>.
  - (iv) By bubbling through H<sub>2</sub>SO<sub>4</sub> when NH<sub>3</sub> is absorbed but not N<sub>2</sub>. Ammonia is recovered by heating the solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> with excess of NaOH.
  - (v) By bubbling through water in which NH<sub>3</sub> dissolves but not PH<sub>3</sub>.
  - (vi) By bubbling through water under high pressure or through NaOH solution in which CO<sub>2</sub> dissolves but not N<sub>2</sub>.
- 13. (i) NH<sub>4</sub>Cl,
  - (ii) N<sub>2</sub>O,
  - (iii)  $Ca(H_2PO_4)_2 \cdot H_2O + 2CaSO_4 \cdot 2H_2O$ ,
  - (iv)  $Ca(H_2PO_4)_2$ ,
  - (v)  $Ca(H_2PO_4)_2 + 2Ca(NO_3)_2$ ,
  - (vi)  $(NH_4)_2SO_4 + NH_4NO_3$ ,
  - (vii) NH<sub>4</sub>NO<sub>3</sub> + CaCO<sub>3</sub>,
  - (viii) (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>,

- (ix) Ca(NO<sub>3</sub>)<sub>2</sub>·NH<sub>4</sub>NO<sub>3</sub>,
- (x)  $CaCN_2 + C$ .

- (c) Single bonds = 12 Double bonds = 4
- (d) Single bonds = 12
- (e) Consult chapter on chemical bonding.
- (f) NH<sub>3</sub> (Pyramidal); NH<sub>4</sub><sup>+</sup> (Tetrahedral); N<sub>2</sub>O (Linear); PCl<sub>3</sub> (Pyramidal); PCl<sub>5</sub> in gaseous state (Triangular bipyramid); NO<sub>3</sub> (Triangular planar); PO<sub>4</sub><sup>3-</sup> (Tetrahedral).
- 15. See text.
- 16. See text.

**Answers : Matching Type Questions** 

## ILLUSTRATIONS OF OBJECTIVE QUESTIONS

- 1. Ammonium nitrate is formed in:
  - (a)  $Zn + v.dil. HNO_3 \longrightarrow$
- (b) Fe + v.dil. HNO<sub>3</sub> $\longrightarrow$
- (c) Sn + dil.  $HNO_3 \longrightarrow$
- (d) All

Ans. (d)

[Hint:  $4M + 10HNO_3 \longrightarrow 4M(NO_3)_2 + NH_4NO_3 + 3H_2O$ ]

- 2. A diatomic gas will be obtained in:
  - (a)  $KNO_3 + K \xrightarrow{Heat}$
- (b)  $NH_4NO_3 \xrightarrow{Heat}$

(c) both

(d) none

Ans. (a)

[Hint:  $2KNO_3 + 10K \longrightarrow 6K_2O + N_2$ ;  $NH_4NO_3 \longrightarrow N_2O + 2H_2O$ ]

Consider the following reaction,

$$NO_2 + NaOH \longrightarrow (A) + (B) + H_2O$$

which of the following is correct?

- (a) both (A) and (B) on heating with Na form  $N_2$
- (b) both (A) and (B) on treatment with Zn and NaOH produce NH<sub>3</sub>
- (c) both are correct
- (d) none is correct

Ans. (c)

[Hint:  $2NO_2 + 2NaOH \longrightarrow NaNO_3 + NaNO_2 + H_2O$ ; (A) (B)  $2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2$ ;  $NaNO_3 + 8H \xrightarrow{Zn/NaOH} NaOH + NH_3 + 2H_2O$ ;  $2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$ ;  $NaNO_2 + 6H \xrightarrow{Zn/NaOH} NaOH + NH_3 + H_2O$ ]

- **4.** Ammonia will be obtained in :
  - (a)  $CaCN_2 + H_2O \longrightarrow$
- (b)  $NH_4H_2PO_4 \xrightarrow{Heat}$
- (c) both
- (d) none

Ans. (c)

[Hint:  $CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$ ;  $NH_4H_2PO_4 \longrightarrow NH_3 + HPO_3 + H_2O$ ]

- 5.  $\text{NaH}_2\text{PO}_4 \xrightarrow{230^{\circ}\text{C}} \text{Na}_3(\text{P}_3\text{O}_9) \xrightarrow{640^{\circ}\text{C}} (\text{NaPO}_3)_n \rightarrow (D)$ compound (D) is:
  - (a) Bunsen's salt
- (b) Graham's salt
- (c) Reimann's salt
- '(d) Werner's salt

Ans. (b)

[ 'int: (D) is sodium hexametaphosphate, (NaPO<sub>3</sub>)<sub>6</sub>, which is called Graham's salt.]

- **6.** The compound  $(SiH_3)_3N$  is expected to be:
  - (a) pyramidal and more basic than (CH<sub>3</sub>)<sub>3</sub>N
  - (b) planar and less basic than (CH<sub>3</sub>)<sub>3</sub>N
  - (c) pyramidal and less basic than (CH<sub>3</sub>)<sub>3</sub>N
  - (d) planar and more basic than (CH<sub>3</sub>)<sub>3</sub>N

Ans. (b)

[Hint:  $(SiH_3)_3N$  is planar and less basic than  $(CH_3)_3N$  because lone pair of N atom is used to form  $d\pi - p\pi$  back bonding with Si-atom.]

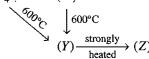
- 7. Which one of the following compounds on strong heating evolves ammonia gas?
  - (a)  $(NH_4)_2Cr_2O_7$
- (b) NH<sub>4</sub>NO<sub>3</sub>
- (c) NH<sub>4</sub>NO<sub>2</sub>
- (d)  $(NH_4)_2SO_4$



Ans. (d)

[Hint:  $(NH_4)_2Cr_2O_7 \longrightarrow N_2$ ;  $NH_4NO_3 \longrightarrow N_2O$ ;  $NH_4NO_2 \longrightarrow N_2$ ;  $(NH_4)_2SO_4 \longrightarrow NH_3$ ]

8.  $H_3PO_4 \xrightarrow{250^{\circ}C} (X)$ 



(X), (Y) and (Z) are:

- (a) H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, HPO<sub>3</sub> and P<sub>4</sub>O<sub>10</sub>
- (b)  $HPO_3$ ,  $H_4P_2O_7$  and  $P_4O_{10}$
- (c) H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>, H<sub>3</sub>PO<sub>3</sub> and P<sub>4</sub>O<sub>6</sub>
- (d) H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>, HPO<sub>3</sub> and P<sub>4</sub>O<sub>6</sub>

Ans. (a)

[Hint: 
$$H_3PO_4 \xrightarrow{250^{\circ}C} H_4P_2O_7 \xrightarrow{600^{\circ}C} HPO_3 \xrightarrow{strongly} P_4O_{10}$$
]

- 9. Solid PCl<sub>5</sub> exists as:
  - (a) dimer P<sub>2</sub>Cl<sub>10</sub>
- (b) [PCl<sub>4</sub>]<sup>+</sup> [PCl<sub>6</sub>]
- (c)  $(PCl_3)(Cl_2)$
- (d) PCl<sub>5</sub> as such

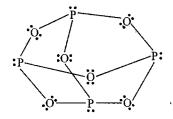
Ans. (b)

- 10. How many P—O bonds and how many lone pairs respectively are present in P<sub>4</sub>O<sub>6</sub> molecule?
  - (a) 12,4

- (b) 8, 8
- (c) 12, 16
- (d) 12, 12

Ans. (c)

[Hint: The structure of P<sub>4</sub>O<sub>6</sub> is the number of P—O bonds and lone pairs are shown. These are 12 and 16 respectively.]



- 11. Which of the following metals, Fe, Zn, Pb, Ag and Pt do not give metal nitrate on treatment with concentrated HNO<sub>3</sub>?
  - (a) Fe and Zn
- (b) Fe and Pt
- (c) Pb, Ag and Pt
- (d) Fe, Ag and Pt

Ans. (b)

- 12. The correct order of bond angle of NO<sub>2</sub><sup>+</sup>, NO<sub>2</sub> and NO<sub>2</sub><sup>-</sup> is: [J.E.E. (Orissa) 2006; C.B.S.E. 2008]
  - (a)  $NO_2^+ < NO_2 < NO_2^-$
- (b)  $NO_2^+ = NO_2^- < NO_2$
- (c)  $NO_2^+ > NO_2 > NO_2^-$
- (d)  $NO_2^+ > NO_2 < NO_2^-$

Ans. (c)

[Hint:







- 13. Which of the following halides is most acidic?
  - (a) PCl<sub>3</sub>

(b) SbCl<sub>3</sub>

(c) BiCl<sub>3</sub>

(d) CCl<sub>4</sub>

Ans. (a)

[Hint: In CCl<sub>4</sub>, carbon atom does not have *d*-orbitals to accommodate a lone pair of electrons and hence is not a Lewis acid. In PCl<sub>3</sub>, SbCl<sub>3</sub> and BiCl<sub>3</sub> central atom has empty *d*-orbitals in each case but electronegativity of P is maximum, hence PCl<sub>3</sub> is strongest acid.]

- 14. Among the following ions,  $p\pi d\pi$  overlap is present in:
  - (a) NO<sub>3</sub>

- (b)  $PO_4^{3}$
- (c)  $CO_3^{2-}$

(d)  $NO_2^-$ 

Ans. (b)



# **OBJECTIVE QUESTIONS**

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**Set I**: This set contains questions with single correct answer.

1.	Which one of the following pairs is obtained on heating		(a) it brings tears to eyes			
	ammonium dichromate? [J.E.E. (W.B.) 2008]		(b) it has high vapour pressure			
	(a) $N_2$ and $H_2O$ $\square$ (b) $N_2O$ and $H_2O$ $\square$		(c) it is corrosive liquid			
	(c) $NO_2$ and $H_2O$ $\square$ (d) $NO$ and $NO_2$ $\square$		(d) it is mild explosive			
2.	By mixing ammonium chloride to potassium nitrite and	14.	Which one of the following oxides of nitrogen is a colo	ured		
	heating, we get: (a) ammonium nitrate $\Box$ (b) KNH <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> $\Box$		gas? (a) N <sub>2</sub> O <sub>2</sub>	П		
	(c) nitrogen $\Box$ (d) nitrogen dioxide $\Box$		(a) $N_2O_2$			
2	The salt which on heating gives a mixture of two gases is:	15.				
Э.	(a) NaNO <sub>3</sub>	15.	(a) NaH <sub>2</sub> PO <sub>2</sub>			
	(a) Nativo <sub>3</sub> $\Box$ (b) $Rivo_3$ $\Box$ (c) $Pb(NO_3)_2$ $\Box$ (d) $NH_4NO_3$ $\Box$		(a) $NaH_2PO_2$ $\Box$ (b) $NaH_2PO_3$ (c) $NaH_2PO_4$ $\Box$ (d) $Na_2HPO_4$			
1	Atomicity of phosphorus is:	16	Ammonia reacts with Nessler's reagent to give:	<b></b>		
ч.	(a) 1	10.	(a) deep blue precipitate $\square$ (b) white precipitate			
-	(c) 3		(c) green precipitate $\Box$ (d) brown precipitate	=		
5	Superphosphate of lime is:	17.				
٠.		1	present in solution is:	auon		
	7 3 7/2 7		(a) $Ag^+$			
	(b) $Ca(H_2PO_4)_2$		(c) $[Ag(NH_3)_2]^+$			
	(c) $Ca(H_2PO_4)_2 \cdot CaSO_4$	18.	When NH <sub>4</sub> OH is added to copper sulphate solution,	***		
	(d) $Ca(H_2PO_4)_2 \cdot H_2O \cdot 2CaSO_4 \cdot 2H_2O$		colour is obtained due to formation of:			
6.	Laughing gas is:		(a) $Cu(NH_3)_4SO_4$ $\Box$ (b) $Cu(NH_4SO_4)_2$			
	(a) NO $\Box$ (b) N <sub>2</sub> O $\Box$		(c) Cu(OH) <sub>2</sub>			
	(c) $N_2O_3$ $\square$ (d) $N_2O_5$ $\square$	19.	· · · · · · · · · · · · · · · · · · ·			
7.	Nitrous oxide is prepared in the laboratory by:		(a) precipitate of yellow colour is formed			
	(a) combination of nitrogen and oxygen $\Box$		(b) phosphorus gets free			
	(b) reduction of NO □		(c) oxide of nitrogen is formed			
	(c) reduction of nitric acid $\Box$		(d) ammonia is evolved			
	(d) thermal decomposition of $NH_4NO_3$	20.	Phosphorus is manufactured by heating in an electric fun	nace		
8. Ammonia is not used:			the mixture of:			
	(a) an anaesthesia		(a) bone ash and coke			
	(b) in medicine	1	(b) bone ash and silica			
	(c) in cold storages		(c) bone ash, silica and coke			
	(d) for preparation of artificial silk		(d) bone ash, NaCl and coke			
9.	Which one of the following is used for drying of ammonia?	21.	Which one of the compound is not known?	_		
	(a) conc. $H_2SO_4$ $\square$ (b) CaO $\square$ (c) $P_2O_5$ $\square$ (d) anhydrous $CaCl_2$ $\square$	1	(a) $NCl_5$			
10	(c) $P_2O_5$ $\square$ (d) anhydrous $CaCl_2$ $\square$ Phosphorus is kept in:	1 22	(c) AsCl <sub>5</sub> $\square$ (d) NCl <sub>3</sub>			
10.	(a) kerosene	22.	Nitrolim is obtained by passing nitrogen over:	<b></b>		
	(c) water		<ul><li>(a) heated mixture of Al<sub>2</sub>O<sub>3</sub> and carbon</li><li>(b) carborundum</li></ul>			
11.		1	• •			
	(a) $N_3H$ $\Box$ (b) $N_2H_4$ $\Box$	23.	(c) calcium carbide	<u></u>		
	(c) NH <sub>3</sub> $\square$ (d) N <sub>4</sub> H <sub>4</sub> $\square$	23.	(a) AsH <sub>3</sub>			
12.	Which one of the following is not used for the manufacture		(a) $Asi i 3$ $\Box$ (b) $Asi i 3$ (c) $H_2O$ $\Box$ (d) $PH_3$			
	of ammonia?	24	A certain element forms a solid oxide which dissolv			
(a) Haber process			water to form an acidic solution. The element is:	V3 III		
	(b) Cyanamide process		(a) S			
	(c) Ammonical mother liquor		(c) Na $\square$ (d) P			
	(d) Solvay ammonia process	25.				
13. It is recommended that ammonia bottles be opened after			with air. The gas X is:			
	cooling in ice for sometime. This is because:		(a) NH <sub>3</sub>			
		1	(c) $N_2O$ $\square$ (d) $NO_2$			

26.	Which one of the following is used as anaesthetic?	41.	Amongst the trihalides of nitrogen, which one is least ba	asic?
	(a) $NH_3$ $\Box$ (b) $N_2O$ $\Box$		(a) $NF_3$	
	(c) NO $\Box$ (d) NO <sub>2</sub> $\Box$		(c) $NBr_3$	
27.	The catalyst used in the manufacture of ammonia by Haber	42.	Which one of the following is the strongest base?	
	process is:	ŀ	(a) $AsH_3$ $\Box$ (b) $SbH_3$	
	(a) Pt $\Box$ (b) Fe $\Box$		(c) $PH_3$ $\square$ (d) $NH_3$	
	(c) Mo $\Box$ (d) $V_2O_5$ $\Box$	43.	Skin becomes yellow in conc. HNO <sub>3</sub> because:	
28.	The catalyst used in the manufacture of NO by Ostwald's	1	(a) the proteins are converted into xanthoproteins	
٠,	process is:		(b) HNO <sub>3</sub> acts as a dehydrating agent	$\Box$
•	(a) Pt		(c) nitrocellulose is formed	
	(c) Mo		(d) HNO <sub>3</sub> acts as an oxidising agent	
29.	The correct order of acidic nature of oxides is:		The number of P-O-P and P-OH bonds pro	esent
	(a) $N_2O_5 < N_2O_3 < NO_2 < NO < N_2O$	1	respectively in pyrophosphoric acid molecule are:	
	(b) $N_2\Theta < N\Theta < N_2O_3 < N\Theta_2 < N_2O_5$		(a) 2,2(b) 1,8	
	(c) $N_2O_5 < N_2O < N_2O_3 < NO < NO_2$	1	(c) $1,4$ $\Box$ (d) $1,2$	
	(d) $NO < N_2O < N_2O_3 < NO_2 < N_2O_5$	45.	Nitrates of all metals are:	
30.	Nitrogen dioxide cannot be obtained by heating:		(a) insoluble in water	
50.	(a) KNO <sub>3</sub>		(c) unstable	
•	(c) $Ca(NO_3)_2$	46.	A gaseous mixture contains O <sub>2</sub> and N <sub>2</sub> in the ratio of 1:	4 by-
31.	Ammonia solution dissolves fairly:	1	mass. The ratio of their molecules is:	•
51.	•		(a) 1:4	
	(a) $Hg_2Cl_2$ $\square$ (b) $PbCl_2$ $\square$ (c) $AgI$ $\square$ (d) $Cu(OH)_2$ $\square$		(c) 3:6	
32.	When ammonia is heated with CO <sub>2</sub> under pressure, the	47.	Which of the following will combine with Fe (II) ion to	form
32.	. <del>-</del>		a brown complex compound?	
	product is: (a) $(NH_4)_2CO_3$ $\square$ (b) $NH_2CONH_2$ $\square$		(a) $N_2O$ $\square$ (b) $NO$	
	(a) $(NH_4)_2CO_3$ $\square$ (b) $NH_2CONH_2$ $\square$ (c) $NH_2COONH_4$ $\square$ (d) $NH_4HCO_3$ $\square$		(c) $N_2O_3$ $\square$ (d) $NO_2$	
22		48.	Red phosphorus is made by heating yellow phosphorus	us in
33.	The percentage of nitrogen in urea is about:		the presence of an inert gas at temperature:	
	(a) 70		(a) 60°C	
24	(c) 47		(c) 240°C	
<i>5</i> 4.	A white precipitate is obtained on hydrolysis of:	49.	Phosphorus is used in:	
	(a) $PCl_5$	1	(a) photography	
25	(c) $BiCl_3$ $\Box$ (d) $AsCl_3$ $\Box$		(c) tubber industry	
<i>3</i> 3.	Industrial preparation of nitric acid by ostwald's process	50.	When phosphine is bubbled through a solution of s	ilver
	involves:		nitrate, is precipitated.	
	(a) oxidation of NH <sub>3</sub> $\square$ (b) reduction of NH <sub>3</sub> $\square$	1	(a) silver	
0.0	(c) hydrogenation of NH <sub>3</sub> □ (d) hydrolysis of NH <sub>3</sub> □		(c) silver oxide $\Box$ (d) none of these	
36.	When treated with nitric acid which of the following liberates	51.	When orthophosphoric acid is heated at 240°C, the	main
	hydrogen?		product formed is:	
	(a) zinc		(a) $HPO_3$ $\Box$ (b) $H_3PO_2$	
<b>~=</b>	(c) magnesium		(c) $H_3PO_3$ $\Box$ (d) $H_4P_2O_7$	
37.	Concentrated nitric acid oxidises cane sugar to:	52.	Complete manure is that which supplies:	
	(a) $CO_2$ and $H_2O$ $\square$ (b) $CO$ and $H_2O$ $\square$		(a) $S$ , $K$ and $N$ $\square$ (b) $N$ , $K$ and $P$	
	(c) CO, CO <sub>2</sub> and H <sub>2</sub> O $\square$ (d) oxalic acid and water $\square$		(c) S and N	
38.	White phosphorus reacts with caustic soda. The products	53.	Superphosphate of lime is obtained by treating:	
	are PH <sub>3</sub> and NaH <sub>2</sub> PO <sub>2</sub> . This reaction is an example of:		(a) calcium phosphate with HCl	
	[B.H.U. 2007]		(b) calcium phosphide with HCl	
	(a) oxidation $\square$ (b) reduction $\square$		(c) calcium phosphate with H <sub>2</sub> SO <sub>4</sub>	
	(c) neutralisation $\Box$ (d) disproportionation $\Box$		(d) calcium phosphate with NaOH	
39.		54.	PH <sub>3</sub> produces smoky rings when it comes in contact	with
	(a) sublimation $\Box$ (b) distillation $\Box$	4	air. This is because:	
	(c) dissolving in $CS_2$ $\square$ (d) heating in air $\square$		(a) it is inflammable	
40.	Which one of the acids is a dibasic acid?	i	(b) it combines with water vapour	
	[P.E.T. (Kerala) 2010]		(c) it combines with nitrogen	
	(a) $H_3PO_3$ $\Box$ (b) $H_3PO_2$ $\Box$		(d) it contains impurity of P <sub>2</sub> H <sub>4</sub>	
	(c) $HPO_2$ $\Box$ (d) $H_2PO_4$ $\Box$	1	<del>-</del> ·	

55.	The metal which becomes passive in contact with con	c.		(c) conc. $HNO_3 + NO_2$	
	HNO <sub>3</sub> is:	_		(d) conc. $HNO_3 + conc. H_2SO_4$	
			68.	The number of steps, in which orthophosphoric acid	1 1S
~~	( )			ionised, are:	
56.	Which gas is obtained when urea reacts with nitrous acid			(a) 1	
	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \		60	(c) 3	Ц
			69.	Phosphorus is usually extracted from:	
57.	Nitrogen percentage is the highest in the fertilizer:			(a) phosphorite	
	•		70	(c) chlorapatite	ш
	( )		/0.	PCl <sub>5</sub> is kept in well stoppered bottles because:	
58.	When zinc reacts with very dilute nitric acid it produces:	_	ļ	<ul><li>(a) it is highly volatile</li><li>(b) it reacts readily with moisture</li></ul>	
	· · · · · · · · · · · · · · · · · · ·			(c) it reacts with oxygen $\Box$ (d) it is explosive	
=0	(-) <u>L</u>		71.		ш
59.	Which of the following-properties-of-white phosphorus a	re		(a) $P_2O_3$ $\square$ (b) $P_2O_4$	
	shared by red phosphorus?			(a) $1_{2}O_{3}$	
			72	Phosphate + conc. HNO <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> soln. $\longrightarrow$ Yell	
			/2.	precipitate. The composition of yellow precipitate is:	IOW
	2				- [7]
	· · · · · · · · · · · · · · · · · · ·		1		ᆸ
60.	The number of P—O—P bridges in the structure of P <sub>4</sub> O	10	72	(c) $(NH_4)_2PO_4\cdot 12MoO_3$ $\square$ (d) $NH_4PO_4\cdot MoO_3$	
	and P <sub>4</sub> O <sub>6</sub> are respectively:		13.	Which one of the materials is not used as a fertilizer	roi
				phosphorus?	<del></del>
				(a) Superphosphate of lime	
61.	Arsenic is detected by:	_		(b) Phosphatic slag	
	_ ``			(c) Guano	
			74	(d) Phosphorite mineral	
62.	Nitrogen molecule is chemically less active because of its		/4.	Which one of the following statements is wrong?	
	83			(a) Ammonia is more poisonous than phosphine	
				(b) Ammonia is more basic than phosphine	
	., 0			(c) Ammonia is more stable than phosphine	
62	(d) stable electronic configuration Which of the following statements is not true?	ш	75	(d) Ammonia is more soluble in water than phosphine	41
05.	(a) Nitrogen differs markedly from the other members of	ita	/5.	One of the acids listed below is formed from P <sub>2</sub> O <sub>3</sub> and	
	- · · · · · · · · · · · · · · · · · · ·			rest are formed from $P_2O_5$ . The acid formed from $P_2O_3$ is	
	•			(a) HPO <sub>3</sub>	
	(c) Nitrogen does not show a greater covalency than thr		76	(c) H <sub>3</sub> PO <sub>4</sub>	ш
	•		/0.	Concentrated nitric acid reacts with iodine to give:  (a) HI	
				(c) $HOIO_2$ $\Box$ (d) $HOIO_3$	
64.	Liquid ammonia is used in refrigerators because:		77.		
	<u> </u>		'''	(a) $SO_4^2$ $\Box$ (b) $SO_3$	
				(a) $50_4$	
				[Hint: $HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + HSO_4^- + H_2O$ ]	
			78.	The reaction between $NH_2$ and $N_2O$ gives :	
65.	The yellow colour often shown by nitric acid can	be	"	(a) NO $\square$ (b) $N_2O_5$	
	removed by:			(c) $NH_2NH_2$ $\square$ (d) $N_3^-$	
	-			[Hint: $NH_2^- + N_2O \longrightarrow N_3^- + H_2O$	
				$NaNH_2 + H_2O \longrightarrow NaOH + NH_3$	
	(c) passing ammonia through acid		79.	,	orus
	(d) adding a little Mg powder			because:	
66.		ast		(a) its colour is red	
	number of moles of KOH?			(b) it is highly polymerised	
	(a) $H_3PO_4$			(c) it is tetratomic	
	$\Box$ (c) $H_3PO_3$ $\Box$ (d) $H_3PO_2$			(d) it is hard	
67.	Aqua-regia is:		80.		iride
*	(a) conc. $HNO_3 + 2$ conc. $HCl$	□.		of nitrous acid?'	
	(b) conc. $HNO_2 + 3$ conc. $HCI$	П	1	•	

	(a) NO	☐ (b) N <sub>2</sub> O <sub>3</sub>		94.	Which of the following f	luorides does not exist?	
	1 7	$\square  \text{(d) } N_2O_5$			(a) NF <sub>5</sub>	□ (b) PF <sub>5</sub>	П
81.		rihalide cannot be hydrolysed?			(c) AsF <sub>5</sub>	$\square  \text{(d) SbF}_5$	
01.	•	☐ (b) PCl <sub>3</sub>		95.	· · ·	over heated CuO, it is oxidised	
	· ·	☐ (d) SbCl <sub>3</sub>		10.	(a) HNO <sub>2</sub>	☐ (b) N <sub>2</sub> O	п.
	/-> ···	oond is stronger than P—O bond.	- 1		(a) 11NO <sub>2</sub> (c) N <sub>2</sub>	$\Box  (d) \text{ NO}_2$	
82.		pitals in the valence shell of ph		96.	· · · -		
OZ.	phorus is:	nais in the valence shell of pi	103-	90.		e isoelectronic. But in contrass	1 10
	(a) 5	□ (b) 3			CN, N <sub>2</sub> is chemically inc	en because or:	
		□ (d) 0			(a) low bond energy	•.	
	(c) 2	□ (a) 0			(b) absence of bond pola		
റാ	[Hint: 5d-orbitals]				(c) unsymmetrical electro		
83.	Which of the following is				<del>-</del>	number of electrons in bond	
	(a) N <sub>3</sub> H	$\square  \text{(b) } N_2H_4$			orbitals		
~4		$\square$ (d)_(CH <sub>3</sub> ) <sub>3</sub> N		97		sed on heating:	
84.		osphide on reaction with excess	s of		(a) $NH_4NO_3$	$\square$ (b) KNO <sub>3</sub>	
	water gives:				(c) NaNO <sub>2</sub>	$\square$ (d) Pb(NO <sub>3</sub> ) <sub>2</sub>	
	(a) one mole of phosphir			98.	Which oxide does not ac		
	(b) two moles of phospho				(a) NO	$\square$ (b) NO <sub>2</sub>	
	(c) two moles of phosph					$\square$ (d) $N_2O_5$	
	(d) two moles of phosph			99.	Of the following, which	h has three electron bond in	its
85.	•	to oxygen bonds in $N_2O_5$ is:	_		structure?		
	(a) 3	□ (b) 4			(a) Nitrous oxide	☐ (b) Dinitrogen trioxide	
	(c) 5	□ (d) 6 ', '			(c) Nitric oxide	☐ (d) Nitrogen pentoxide	
	O <sub>2</sub> 1	5 70		100.	When AgNO <sub>3</sub> is heated	strongly, the products formed	are:
	[Hint: $\frac{O_{1}}{2}N \stackrel{3}{=} O \stackrel{4}{=} 1$	v. 1			(a) NO and NO <sub>2</sub>		
	0 2	60			(c) $NO_2$ and $O_2$	$\square$ (d) NO and O <sub>2</sub>	
86.	Which one of the following	ing cations does not form comp	olex	101.	*		* 4
	with ammonia?				(a) H <sup>+</sup>	□ (b) OH _	
	(a) Ag <sup>+</sup>	☐ (b) Cu <sup>2+</sup>			(c) $NH_4^+$	$\Box$ (d) NH <sub>4</sub> and OH	
	(c) Cd <sup>2+</sup>	$\square$ (d) $Pb^{2+}$		102.	Each of the following is	s true of white and red phospho	orus
87.		acid is heated, it decompose	s to		except:		_
	give:				(a) both are soluble in (		
	(a) oxygen and nitrogen				(b) consist of same kind		
	(b) nitric oxide				(c) can be oxidised by h		
	(c) oxygen				(d) can be converted to		
	(d) nitrogen dioxide and	oxygen		103.		oiling point than PH <sub>3</sub> , because	
88.	- ·	of oxygen atoms bonded to o	each		(a) NH <sub>3</sub> has much higher		
	phosphorus atom is:	· -			(b) NH <sub>3</sub> forms hydrogen		
	(a) 2.5	□ (b) 3				bonds while PH <sub>3</sub> contains cova	lent
	(c) 4	□ (d) 5			bonds		
89.	When bismuth chloride	is poured into a large volume	e of		(d) NH <sub>3</sub> undergoes umb		
	water, the white precipita	ate produced is:		104.	PCl <sub>3</sub> reacts with water to		
	(a) Bi(OH) <sub>3</sub>	☐ (b) Bi <sub>2</sub> O <sub>3</sub>			(a) PH <sub>3</sub>	$\Box$ (b) H <sub>3</sub> PO <sub>3</sub> and HCl	
	(c) Bi <sub>2</sub> Cl <sub>8</sub>	☐ (d) BiOCl			(c) POCl <sub>3</sub>	$\square$ (d) H <sub>3</sub> PO <sub>4</sub>	
90.	Which of the following e	elements is metallic?		105.	•	H <sub>2</sub> SO <sub>4</sub> , phosphorus changes to	
	(a) P	□ (b) As			(a) phosphorus acid	☐ (b) metaphosphoric acid	
	(c) Sb	□ (d) Bi				id 🗆 (d) pyrophosphoric acid	
91.	Which one has the lowe	est boiling point?		106.	Mixture used in Holme'		
	(a) NH <sub>3</sub>	☐ (b) PH <sub>3</sub>			(a) CaC <sub>2</sub> and CaCl <sub>2</sub>	$\Box$ (b) CaCl <sub>2</sub> and Ca <sub>3</sub> P <sub>2</sub>	
	(c) AsH <sub>3</sub>	☐ (d) SbH <sub>3</sub>			(c) CaC <sub>2</sub> and Ca <sub>3</sub> N <sub>2</sub>	$\Box$ (d) CaC <sub>2</sub> and Ca <sub>3</sub> P <sub>2</sub>	
92.	The most stable hydride			107.	Blasting of TNT is done	•	
	(a) NH <sub>3</sub>	□ (b) PH <sub>3</sub>		-	(a) NH <sub>4</sub> Cl	$\Box$ (b) NH <sub>4</sub> NO <sub>3</sub>	
	(c) AsH <sub>3</sub>	□ (d) SbH <sub>3</sub>		ŧ	(c) $NH_4NO_2$	$\Box$ (d) $(NH_4)_2SO_4$	
93.				108.		iven below, the correct decrea	sing
	(a) NCl <sub>3</sub>	☐ (b) PCl <sub>3</sub>			order of acid strength is		
	(c) AsCl-	□ (d) di			(i) H <sub>2</sub> AsO <sub>4</sub> (ii) H <sub>2</sub> SbO	$_4$ (iii) HNO <sub>3</sub> (iv) H <sub>3</sub> PO <sub>4</sub>	

	(a) $(iv) > (iii) > (i)$ (b) $(iii) > (iv) > (i) > (ii)$		120.	A metal X on heating in nitrogen gas gives Y. Y or	n treatment
	(c) $(iii) > (ii) > (iv) > (i)$			with H <sub>2</sub> O gives a colourless gas which when pass	ed through
109.	Among the following oxides, the lowest acidic is:			CuSO <sub>4</sub> solution gives a blue colour. Y is: [D	.C.E. 2000]
	(a) $P_4O_6$			(a) $Mg(NO_3)_2$ $\square$ (b) $Mg_3N_2$	
	(c) $As_4O_6$			(c) NH <sub>3</sub>	
110.	The basic character of the hydrides of Vth group elements		121.	In which of the following the bond angle is max	
	decreases in the order:				.S.E. 2001]
	(a) $NH_3 > PH_3 > AsH_3 > SbH_3$			(a) $NH_3$ $\square$ (b) $NH_4^+$	
	(b) $SbH_3 > AsH_3 > PH_3 > NH_3$			(c) $PCl_3$	ā
	(c) $NH_3 > NBH_3 > PH_3 > AsH_3$		122	Nitrogen forms N <sub>2</sub> but phosphorus is converted in	
	(d) $SbH_3 > PH_3 > AsH_3 > NH_3$		I.LaL.		.S.E. 2001]
111	Solid PCl <sub>5</sub> exists as:	<u></u>		(a) triple bond is present between phosphorus	
111.				(b) $p\pi$ - $p\pi$ bonding is weak	
	(a) $[PCl_4]^+[PCl_6]^ \Box$ (b) dimer $P_2Cl_{10}$			(c) $p\pi$ - $p\pi$ bonding is strong	
	(c) $[PCl_3][Cl_2]$ $\square$ (d) $PCl_5$ as such			(d) multiple bond is formed easily	
112.	Which of the following species is paramagnetic?		122	•	. —
	(a) $O_2^{2-}$		123.	In NO <sub>3</sub> ion, the number of bond pair and lo	ne pan or
	(c) CO $\square$ (d) CN $^{-}$			electrons on nitrogen atoms are:	N.C. 2002]
113.	The BCl <sub>3</sub> is a planar molecule whereas, NCl <sub>3</sub> is pyram	idal		[C.B.S.E. 2002; A.F.	
	because:			(a) 2, 2	
	(a) N—Cl bond is more covalent than B—Cl bond		124	(c) 1,3	
	(b) B—Cl bond is more polar than N—Cl bond		124.	A pale blue liquid which is obtained by reacting	•
	(c) hitrogen atom is smaller than boron				[I.I.T. 2008]
	(d) BCl <sub>3</sub> has no lone pair but NCl <sub>3</sub> has a lone pair of elec	tron		(a) $N_2O_3$	
				(c) $N_2O_4$	
114.	Nitrogen can be purified from the impurities of oxide	s of		[Hint: NO + NO <sub>2</sub> $\xrightarrow{-30^{\circ}\text{C}}$ N <sub>2</sub> O <sub>3</sub> (Pale blue)]	
	nitrogen and ammonia by passing through:		125.	The element which forms oxides in all the oxid	ation states
	(a) a solution of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> acidified with H <sub>2</sub> SO <sub>4</sub>				.M.S. 2004]
	(b) concentrated HCl			(a) N	o o
	(c) alkaline solution of pyrogallol			(c) As	
	(d) a solution of KOH		126.		
115.	In white phosphorus (P <sub>4</sub> ) molecule which one is not corr		120.		[I.I.T. 2004]
	(a) Six P—P single bonds are present		-	-	[1.1.1. 2004]
	(b) Four P—P single bonds are present			(a) heating NH <sub>4</sub> NO <sub>2</sub>	
	(c) Four lone pairs of electron are present			(b) heating NH <sub>4</sub> NO <sub>3</sub>	
	(d) P P P bond angle is 60°			(c) treating Mg <sub>3</sub> N <sub>2</sub> with H <sub>2</sub> O	
116.	Which of the following is the correct statement for PF		2	(d) heating H <sub>2</sub> O <sub>2</sub> on NaNO <sub>2</sub>	
	(a) It is less basic than NH <sub>3</sub>		127.	Which one of the following oxides of nitrogen	
	(b) It is less poisonous than NH <sub>3</sub>				.M.C. 2004]
	(c) Electronegativity of PH <sub>3</sub> is greater than NH <sub>3</sub>			(a) $NO_2$ $\square$ (b) $N_2O$	
	(d) It does not show reducing properties			(c) $N_2O_3$ $\square$ (d) $N_2O_5$	
117.	The number of P—O—P bonds in cyclic metaphosph	oric	128.	In the electrothermal process, the compound di	
	acid is:	_		silica from calcium phosphate is : [C.E.T. (Karns	ataka) 2004]
	(a) zero $\Box$ (b) two			(a) calcium phosphide	
	(c) three $\Box$ (d) four			(b) phosphine	
118.	The hybridization of atomic orbitals of nitrogen in $NO_2^+$ ,	_		(c) phosphorus	
	and NH <sub>4</sub> are: [L.I.T. (S) 2	<i>(</i> 000]		(d) phosphorus pentoxide	
	(a) $sp$ , $sp^3$ and $sp^2$ respectively		129.	N <sub>2</sub> forms NCl <sub>3</sub> whereas P can form both PCl <sub>3</sub>	and PCl <sub>5</sub> .
	(b) $sp$ , $sp^2$ and $sp^3$ respectively				rissa) 2004]
	(c) $sp^2$ , $sp$ and $sp^3$ respectively			(a) P has d-orbitals which can be used for bond	ling but N <sub>2</sub>
	(d) $sp^2$ , $sp^3$ and $sp$ respectively			does not have	Ī
110		-	1		
119.		20001		(b) N atom is larger than P in size	
119.	Ammonia can be dried by: [I.I.T. (S) 2 (a) conc. $H_2SO_4$ $\square$ (b) $P_4O_{10}$	[000		<ul><li>(b) N atom is larger than P in size</li><li>(c) P is more reactive towards Cl than N</li></ul>	

130.	Which is used to produce smoke screens? [A.F.M.C. 2005]	140.	Match List-I with List-II and select the correct answer:
	(a) Zinc sulphide $\square$ (b) Calcium phosphide $\square$		[J.E.E. (Orissa) 2008]
	(c) Zinc phosphide		List-II List-II
131.	The percentage of p-character in the orbitals forming P-P		(Molecules) (Boiling points)
	bonds in $P_4$ is: [I.I.T. 2007]		(A) $NH_3$ (1) $290 K$
	(a) 25		(B) PH <sub>3</sub> (2) 211 K
	(c) 50		(C) $AsH_3$ (3) $186 K$
132.	Which of the following is the correct order of increasing		(D) SbH <sub>3</sub> (4) 264 K
	enthalpy of vaporisation? [P.M.T. (Kerala) 2007]	}	(E) BiH <sub>3</sub> (5) 240 K
	(a) $NH_3 < PH_3 < AsH_3$ $\square$ (b) $AsH_3 < PH_3 < NH_3$ $\square$		(a) A-3, B-2, C-5, D-4, E-1
		1	(b) A-5, B-3, C-2, D-4, E-1
			(c) A-1, B-4, C-5, D-2, E-3
100	(e) $AsH_3 < NH_3 < PH_3$		(d) A-1, B-2, C-3, D-4, E-5
133.	Chlorine reacts with excess of ammonia to form:	141	Phosphine, acetylene and ammonia ean be formed by
	[P.M.T. (Kerala) 2007]	171.	<u>.</u>
	(a) $NH_4Cl$ $\Box$ (b) $N_2 + HCl$ $\Box$		=
	(c) $N_2 + NH_4Cl$ $\square$ (d) $N_2 + NCl_3$ $\square$		(a) $Mg_3P_2$ , $Al_4C_3$ , $Li_3N$
	(e) $NCl_3 + HCl$		(b) $Ca_3P_2$ , $CaC_2$ , $Mg_3N_2$
134.	The following are some statements related to VA group	l · .	(c) $Ca_3P_2$ , $CaC_2$ , $CaCN_2$
	hydrides,	1.40	(d) $Ca_3P_2$ , $Mg_2C$ , $NH_4NO_3$
	(i) Reducing property increases from NH <sub>3</sub> to BiH <sub>3</sub>	142.	The number of P—O bonds and lone pair of electrons
	(ii) Tendency to donate lone pair decreases from NH <sub>3</sub> to		present in P <sub>4</sub> O <sub>6</sub> molecule are, respectively:
	BiH <sub>3</sub>	}	[E.A.M.C.E.T. 2008]
	(iii) Thermal stability of hydrides decreases from NH <sub>3</sub> to		(a) 12, 16
	$BiH_3$		(c) 8, 8
	(iv) Bond angle decreases from NH <sub>3</sub> to BiH <sub>3</sub>	143.	Hydrolysis of NCl <sub>3</sub> gives NH <sub>3</sub> and X. Which of the following
	The correct statements are: [E.A.M.C.E.T. (Engg.) 2007]		is X? [A.F.M.C. 2008]
	(a) (i), (ii), (iii) and (iv) $\square$ (b) (i), (iii) and (iv) $\square$		(a) HClO <sub>4</sub>
-	(c) (i), (ii) and (iv) $\Box$ (d) (i) and (iv) $\Box$		(c) HClO $\Box$ (d) HClO <sub>2</sub> $\Box$
135.	Which is in the decreasing order of boiling points of	144.	The shape of PCl <sub>3</sub> molecule is: [A.F.M.C. 2008]
	V group hydrides? [E.A.M.C.E.T. (Med.) 2007]		(a) trigonal bipyramidal  (b) tetrahedral
	(a) $NH_3 > PH_3 > AsH_3 > SbH_3$		(c) pyramidal
	(b) $SbH_3 > AsH_3 > PH_3 > NH_3$	145.	Which of the following is not correct? [C.P.M.T. 2008]
	(c) $PH_3 > NH_3 > AsH_3 > SbH_3$		(a) Hydrolysis of NCl <sub>3</sub> gives NH <sub>3</sub> and HClO
	(d) $SbH_3 > NH_3 > AsH_3 > PH_3$		(b) NH <sub>3</sub> is less stable than PH <sub>3</sub>
136.	N <sub>2</sub> O is isoelectronic with CO <sub>2</sub> and N <sub>3</sub> , which is the structure		(c) NH <sub>3</sub> is a weak reducing agent compared to PH <sub>3</sub>
	of $N_2O$ ? [J.E.E. (Orissa) 2007]	1	(d) Nitric oxide in solid state exhibits diamagnetic property
	(a) N	146.	The atomicity of phosphorus is $X$ and the PPP bond angle
	_ · · · · · · · ·		is Y. What are X and Y? [D.C.E. (Engg.) 2008]
	(c) $N^N$ O $\square$ (d) $N_N$ $\square$	1	(a) $X = 4$ , $Y = 90^{\circ}$
137.	The hybridization state of the central atom in PCl <sub>5</sub> is:		(c) $X = 3$ , $Y = 120^{\circ}$
	[D.C.E. (Engg.) 2007]	147.	The reaction of $P_4$ with X leads selectively to $P_4O_6$ . The X
	(a) $sp^3d$		is: [L.I.T. 2009]
	(c) $sp^3$ $\Box$ (d) $d^2sp^3$ $\Box$		(a) a dry O <sub>2</sub>
138.	Cl—P—Cl bond angles in PCl <sub>5</sub> molecule are:		(b) a mixture of $O_2$ and $N_2$
156.	- ·		(c) moist O <sub>2</sub>
	[V.I.T.E.E. 2008]		(d) O <sub>2</sub> in presence of aqueous NaOH
	(a) 120° and 90°		[Hint: N <sub>2</sub> prevents the further reaction of P <sub>4</sub> O <sub>6</sub> into P <sub>4</sub> O <sub>10</sub> .]
120	(c) 60° and 120°	148.	Atoms in P <sub>4</sub> molecule of white phosphorus are arranged
139.	Bond angles of NH <sub>3</sub> , PH <sub>3</sub> , AsH <sub>3</sub> and SbH <sub>3</sub> are in the order:	0.	regularly in the following way: [J.E.E. (W.B.) 2009]
	[J.E.E. (Orissa) 2008]		(a) at the corners of a cube
	(a) $PH_3 > AsH_3 > SbH_3 > NH_3$		(b) at the corners of an octahedron
	(b) $SbH_3 > AsH_3 > PH_3 > NH_3$		// · · · · · · · · · · · · · · · · · ·
	(c) $SbH_3 > AsH_3 > NH_3 > PH_3$	(	(d) at the corners of a tetrahedron (d) at the centre and corners of a tetrahedron
	(d) $NH_3 > PH_3 > AsH_3 > SbH_3$	t .	(a) at the contact and corners of a terraneuron

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Elements	of	Group	VA	or	15	(Elements	of	Nitrogen	and	Phos	phorus	Fa	mily	1

			the state of the s
Elem	ents of Group VA or 15 (Elements of Nitrogen and Phospho	orus Fa	mily) <b>523</b>
150. 151.	Correct order of bond angles for the following is :   [J.E.E. (Orissa) 2009]  (a) $NH_3 > PCl_3 > BCl_3$	152.	(a) 6
	I: The following questions may have more than one		•
155.	Nitrogen (I) oxide is produced by:  (a) thermal decomposition of ammonium nitrate  (b) disproportionation of $N_2O_4$ (c) thermal decomposition of ammonium nitrite  (d) interaction of hydroxylamine and nitrous acid	160. 161.	1.7
154.	Ammonia on reaction with hypochlorite anion can form:  [I.I.T. 1999]  (a) NO	162.	(a) N
155.	(c) $N_2H_2$ $\square$ (d) $HNO_2$ $\square$ Which of the following metals become passive when dropped into conc. $HNO_3$ ?  (a) $Cu$ $\square$ (b) $Fe$ $\square$ (c) $Cr$ $\square$ (d) $Al$ $\square$	1/2	(a) White $P + Ca(OH)_2 \longrightarrow$ (b) $AlP + H_2O \longrightarrow$ (c) $H_3PO_4 \xrightarrow{Heat}$ (d) $PH_4I + NaOH \longrightarrow$
156.	White phosphorus has:  (a) six P—P single bonds  (b) four P—P single bonds  (c) four lone pairs of electrons  (d) P P P angle of 60°   [I.I.T. 1998]  [I.I.T. 1998]	163.	A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is(are):  [I.I.T. 2008]  (a) NH <sub>4</sub> NO <sub>3</sub>
157.	Which of the following substances are used as fertilizers?  (a) Nitrolim  (b) Urea  (c) Superphosphate of lime  (d) Phosphorite mineral		(c) $NH_4Cl$ $\square$ (d) $(NH_4)_2SO_4$ $\square$ [Hint: $NH_4NO_3 + NaOH \longrightarrow NH_3 + NaNO_3 + H_2O$ [H] $Non-flammable$ $gas$ $NaNO_3 + 4Zn + 7NaOH \longrightarrow 4Na_2ZnO_2 + NH_3 + 2H_2O$
158.	Which elements of group 15 are metalloids?  (a) P □ (b) As □  (c) Sb □ (d) Bi □	164	$NH_4NO_2 + NaOH \longrightarrow NH_3 + NaNO_2 + H_2O$ [H] $3Zn + 5NaOH + NaNO_2 \longrightarrow 3Na_2ZnO_2 + NH_3 + H_2O$ ]  The mitrogen equid (a) that contain(a) N. N. N. hand(a) in(cas)
159.	The metals which produce hydrogen only with very dilute nitric acid are:  (a) Zn □ (b) Sn □  (c) Mg □ (d) Mn □	164.	The nitrogen oxide(s) that contain(s) N—N bond(s) is(are): [I.I.T. 2009]  (a) N <sub>2</sub> O $\Box$ (b) N <sub>2</sub> O <sub>3</sub> $\Box$ (c) N <sub>2</sub> O <sub>4</sub> $\Box$ (d) N <sub>2</sub> O <sub>5</sub> $\Box$ [Hint: N <sub>2</sub> O : N=N=O $\longleftrightarrow$ N=N—O $O$ $O$ $O$ $O$ $O$ $O$ $O$ $O$ $O$
	•	I	-0 0 •0

2	tusi	vers									-								
1.	(a)	2.	(c)	3.	(c)	4.	(d)	5.	(d)	6.	(b)	7.	(d)	8.	(a) ·	9.	(b)	10.	(c)
11.	(a)	12.	(d)	13.	(b)	14.	(b)	15.	(a)	16.	(d)	17.	(c)	18.	(a)	19,	(c)	20.	(c)
21.	(a)	22.	(c)	23.	(b)	24.	(d)	25.	(b)	26.	(b)	27.	(b)	28.	(a)	29.	(b)	30.	(a)
31.	(d)	32.	(b)	33.	(c)	34.	(c)	35.	(a)	36.	(c)	37.	(d)	38.	(d)	39.	(c)	40.	(a)
41.	(a)	42.	(d)	43.	(a)	44.	(c)	45.	(b)	46.	(d)	47.	(b)	48.	(c)	49.	(d)	50.	(b)
51.	(d)	52.	(b)	53.	(c)	54.	(d)	55.	(b)	56.	(a)	57.	(c)	58.	(a)	59.	(b)	60.	(c)
61.	(d)	62.	(b)	63.	(c)	64.	(d)	65.	(a)	66.	(d)	67.	(b)	68.	(c)	69.	(a)	70.	(b)
71.	(c)	72.	(b)	73.	(d)	74.	(a)	75.	(d)	76.	(c)	77.	(d)	<b>78.</b>	(d)	79.	(b)	80.	(b)
81.	(a)	82.	(a)	83.	(a)	84.	(d)	85.	(d)	86.	(d)	87.	(d)	88.	(c)	89.	(d)	90.	(d)
91.	(b)	92.	(a)	93.	(a)	94.	(a)	95.	(c)	96.	(b)	97.	(d)	98.	(d)	99.	(c)	100.	(c)
101.	(d)	102.	(a)	103.	(b)	104.	(b)	105.	(c)	106.	(d)	107.	(b)	108.	(b)	109.	(c)	110.	(a)
111.	(a)	112.	(b)	113.	(d)	114.	(d)	115.	(b)	116.	(a)	117.	(c)	118.	(b)	119.	(c)	120.	(b)
121.	(b)	122.	(b)	123.	(d)	124.	(a)	125.	(a)	126.	(a)	127.	(d)	128.	(d)	129.	(a)	130.	(b)
131.	(d)	132.	(c)	133.	(c)	134.	(a)	135.	(d)	136.	(d)	137.	(a)	138.	(a)	139.	(d)	140.	(b)
141.	(b)	142.	(a)	143.	(c)	144.	(c)	145.	(b)	146.	(b)	147.	(b)	148.	(c)	149.	(b)	150.	(a)
151.	(a)	152.	(a)	153.	(a,d)	154.	(b,c)	155.	(b,c,d)	156.	(a,c,d)	157.	(a,b,c)	158.	(b,c)	159.	(c,d)	160.	(a,b)
161.	(b,c)	162.	(a,b,d)	163.	(a,b)	164.	(a,b,c)												

## **Objective Questions for IIT ASPIRANTS**



- 1. White phosphorus on reaction with limewater gives calcium salt of an acid (A) along with a gas (X). Which of the following is correct?
  - (a) (A) on heating gives (X) and  $O_2$
  - (b) The bond angle in (X) is less than that in case of ammonia
  - (c) (A) is a dibasic acid
  - (d) (X) is more basic than ammonia

[Hint: 
$$8P + 3Ca(OH)_2 + 6H_2O \longrightarrow 3Ca(H_2PO_2)_2 + 2PH_3$$
(X)

- (A) is H<sub>3</sub>PO<sub>2</sub> (Hypophosphorus acid). It is a monobasic acid. PH<sub>3</sub> is less basic than NH<sub>3</sub>. The bond angle in (X) is less than that present in NH<sub>3</sub>. H<sub>3</sub>PO<sub>2</sub> on heating gives orthophosphoric acid and phosphine (X).]
- 2. One mole of H<sub>3</sub>PO<sub>3</sub> on reaction with excess of NaOH gives:
  - (a) one mole of Na<sub>2</sub>HPO<sub>3</sub>
  - (b) two moles of Na<sub>2</sub>H<sub>2</sub>PO<sub>3</sub>
  - (c) two moles of Na<sub>2</sub>HPO<sub>3</sub>
  - (d) one mole of Na<sub>3</sub>PO<sub>3</sub>

[Hint: 
$$H_3PO_3 + 2NaOH \longrightarrow Na_2HPO_3 + 2H_2O$$
]

- 3. A diatomic gas will be obtained in:
  - (a) Cu + dil.  $HNO_3 \longrightarrow$
  - (b)  $(NH_4)_2Cr_2O_7 \xrightarrow{Heat}$
  - (c) both
  - (d) none

[Hint: 
$$3\text{Cu} + 8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O};$$
  
 $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}]$ 

**4.** For NH<sub>2</sub>OH·HCl + NaNO<sub>2</sub>  $\longrightarrow$  (A)  $\xrightarrow{\text{Cu}}$  (B) + (X)<sub>gas</sub>, which of the following is correct?

- (a) (B) is an amphoteric oxide
- (b) (X) is a colourless, diamagnetic gas which combines with Al on heating
- (c) (X) can be produced by action of (Zn + NaOH) on NaNO<sub>2</sub>
- (d) none of the above

[Hint: 
$$NH_2OH \cdot HCl + NaNO_2 \longrightarrow N_2O \xrightarrow{Cu} CuO + N_2 (B) (X)$$
  
CuO is a basic oxide.  $N_2$  is a colourless, diamagnetic gas which combines with Al.  $2Al + N_2 \longrightarrow 2AlN$ .  
 $Zn + NaOH \cdot evolves \cdot H_2 \cdot which reduces \cdot NaNO_2 \cdot to form NH_3 \cdot gas. NaNO_2 + 6H \longrightarrow NaOH + NH_3 + H_2O.]$ 

- 5. If O<sub>2</sub> is removed from the formula of anhydride of HNO<sub>2</sub>, then the formula of the resulting compound satisfies which of the following properties?
  - (a) It produces tears in eyes (b) It supports combustion
  - (c) It is paramagnetic
  - (d) It cannot react with red hot copper
  - [Hint: The anhydride of HNO<sub>2</sub> is N<sub>2</sub>O<sub>3</sub>. If O<sub>2</sub> is removed, then the resulting compound is N<sub>2</sub>O. Nitrous acid does not produce tears in eyes and it is diamagnetic in nature. It supports combustion and reacts with hot copper.]
- 6. Which of the following is correct?
  - (a) N<sub>2</sub>O is a laughing gas and is angular in shape
  - (b) NO2 is a sweet smelling and is angular in shape
  - (c) NO is a colourless gas and acidic in nature
  - (d) NO<sub>2</sub> on reaction with NaOH gives a mixture of two salts

[Hint: N<sub>2</sub>O is a laughing gas and linear in shape. NO<sub>2</sub> is having pungent odour and angular in shape. NO is a colourless and neutral in nature. NO<sub>2</sub> on reaction with NaOH forms two salts NaNO<sub>2</sub> and NaNO<sub>3</sub>.

$$2NaOH + 2NO_2 \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

- 7. When a mixture of NO and NO<sub>2</sub> is passed through an aqueous solution of ammonium sulphate, we get:
  - (a) a dibasic acid which has no dehydrating property
  - (b) a diatomic gas which on reaction with acetylene under electric spark gives a monobasic acid whose anion is pseudohalide
  - (c) a dibasic acid whose dinegative anion has all bonds equal with bond angle 90°
  - (d) a dibasic acid whose anhydride in solid state forms a cyclic trimer

[Hint: NO + NO<sub>2</sub> + (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O 
$$\rightarrow$$
 2NH<sub>4</sub>NO<sub>2</sub>+ H<sub>2</sub>SO<sub>4</sub>  $\downarrow$  2N<sub>2</sub> + 4H<sub>2</sub>O

$$N_2 + C_2H_2 \xrightarrow{\text{Electric}} 2HCN$$
  
CN is a pseudohalide.]

- Copper metal on treatment with dilute HNO3 produces a gas (X). (X) when passed through acidic solution of stannous chloride, a nitrogen containing compound (Y) is obtained. (Y) on reaction with nitrous acid produces a gas (Z). Gas (Z)is:
  - (a) NO

(b)  $N_2$ 

(c) NO<sub>2</sub>

(d)  $N_2O$ 

(c) NO<sub>2</sub> (d) N<sub>2</sub>O  
[Hint: Cu+dil.HNO<sub>3</sub> 
$$\rightarrow$$
 NO  $\xrightarrow{SnCl_2/HCl}$  NH<sub>2</sub>OH·HCl  $\xrightarrow{(Y)}$   $\xrightarrow{HNO_2}$  N<sub>2</sub>O] (Z)

- 9. A tetra-atomic molecule (A) on reaction with nitrogen (I) oxide, produces two substances (B) and (C). (B) is a dehydrating agent while substance (C) is a diatomic gas which shows almost inert behaviour. The substances (A), (B) and (C) are:
  - (a)  $P_4$ ,  $P_4O_{10}$ ,  $N_2$

(b)  $P_4$ ,  $N_2O_5$ ,  $N_2$ 

(c)  $P_4, P_2O_3, Ar$ 

(d)  $P_4, P_2O_3, O_2$ 

[Hint: 
$$P_4 + 10N_2O \longrightarrow P_4O_{10} + 10N_2$$
]

- 10. The number of P—O—P and P—O—H bonds present respectively in pyrophosphoric acid molecule are:
  - (a) 1, 2

(b) 2, 2

(c) 1, 4

(d) 1, 8

[Hint: The structure of pyrophosphoric acid is

There are one P-O-P and four P-O-H bonds.]

- 11. Which of the following is a cyclic oxoacid?
  - (a)  $H_4P_2O_7$

(b)  $H_4P_2O_6$ 

(c)  $H_5P_5O_{15}$ 

(d)  $H_3P_3Q_9$ 

[Hint: H<sub>3</sub>P<sub>3</sub>O<sub>9</sub> is a cyclic trimetaphosphoric acid.

12. The equivalent mass of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) in the reaction, NaOH +  $H_3PO_4 \longrightarrow NaH_2PO_4 + H_2O_5$ , is:

(a) 25

(b) 49

(c) 59

(d) 98

[Hint: Only one hydrogen atom of H<sub>3</sub>PO<sub>4</sub> is replaced, so its equivalent mass is equal to its molecular mass.]

13. The oxyacid of phosphorus in which phosphorus has the lowest oxidation state is:

(a) hypophosphorus acid

(b) orthophosphoric acid

(c) pyrophosphoric acid

(d) metaphosphoric acid

[Hint: 
$$H_3PO_2$$
, O.S.  $P = +1$ ;  $H_3PO_4$ , O.S.  $P = +5$ ;  $H_4P_2O_7$ , O.S.  $P = +5$ ;  $HPO_3$ , O.S.  $P = +5$ ]

- 14. Which is/are correct statements about P<sub>4</sub>O<sub>6</sub> and P<sub>4</sub>O<sub>10</sub>?
  - (a) Both form oxoacids H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> respectively
  - (b) In P<sub>4</sub>O<sub>6</sub> each P is joined to three O and in P<sub>4</sub>O<sub>10</sub> each P is linked to four O atoms
  - (c) Both
  - (d) None
- 15. Blue liquid which is formed at -30°C by mixing of two gases is:

(a) N<sub>2</sub>O

(b)  $N_2O_5$ 

(c)  $N_2O_3$ 

(d)  $N_2O_4$ 

[Hint: NO+NO<sub>2</sub>  $\xrightarrow{-30^{\circ}\text{C}}$  N<sub>2</sub>O<sub>3</sub> (Pale blue colour)]

- 16. For H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>, the correct choice is:
  - (a) H<sub>3</sub>PO<sub>3</sub> is dibasic and reducing
  - (b) H<sub>3</sub>PO<sub>3</sub> is dibasic and non-reducing
  - (c) H<sub>3</sub>PO<sub>4</sub> is tribasic and reducing
  - (d) H<sub>3</sub>PO<sub>3</sub> is tribasic and non-reducing
- 17. The compound molecular in nature in gas phase but ionic in solid state is:
  - (a) PCl<sub>3</sub>

(b) CCl<sub>4</sub>

(c) PCl<sub>5</sub>

(d) POCl<sub>3</sub>

[Hint: PCl<sub>5</sub> exists as [PCl<sub>4</sub>]<sup>+</sup>[PCl<sub>6</sub>] in solid state.]

- 18. The decreasing order of the boiling points of the following hydrides is:
  - (i)  $NH_3$  (ii)  $PH_3$  (iii)  $AsH_3$  (iv)  $SbH_3$  (v)  $H_2O$
  - (a) (v) > (iv) > (i) > (iii) > (ii)
  - (b) (v) > (i) > (ii) > (iii) > (iv)
  - (c) (ii) > (iv) > (iii) > (i) > (v)
  - (d) (iv) > (iii) > (i) > (ii) > (v)

[Hint: B.pts:  $NH_3 = -33^{\circ}C$ ;  $PH_3 = -89^{\circ}C$ ;  $AsH_3 = -63$ ;  $SbH_3 = -9$ ;  $H_2O = 100^{\circ}C$ 

**4.** (b) 1. (b) 3. (c) 5. (b) **6.** (d) 7. (b) 8. (d) **2.** (a) **9.** (a) 10. (c) 11. (d) **12.** (d) 17. (c) 13. (a) 14. (c) 15. (c) 16. (a) 18. (a)

## **Assertion-Reason Type Questions**

The following questions consist of two statements as Assertion (A) and Reason (R). While answering these questions choose correctly any one of the following responses.

- (a) If both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) If (A) is true but (R) is false.
- (d) If (A) is false but (R) is true.
- (e) If both (A) and (R) are false.
- 1. (A) HNO<sub>3</sub> is stronger than HNO<sub>2</sub>.
  - (R) In HNO<sub>3</sub> there are two nitrogen to oxygen bonds whereas in HNO<sub>2</sub> there is only one. [I.I.T. 1998]
- 2. (A)  $P_4$  is more reactive than  $N_2$ .
  - (R) P—P single bond is much more weaker as compared toN≡N triple bond.
- 3. (A) Although PF<sub>5</sub>, PCl<sub>5</sub> and PBr<sub>5</sub> are known, the pentahalides of nitrogen have not been observed.
  - (R) Phosphorus has lower electronegativity than nitrogen.
    [I.I.T. 1995]

**4.** (A) Nitrogen is unreactive at room temperature but becomes reactive at elevated temperatures or in presence of a catalyst.

(R) In nitrogen molecule, there is extensive delocalization of electrons. [A.I.I.M.S. 1996]

- 5. (A) PH<sub>3</sub> is more basic than NH<sub>3</sub>.
  - (R) Electronegativity of N is more than phosphorus.
- (A) H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> are tribasic acids as they contain three hydrogen atoms each.
  - (R) Both H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> are reducing in nature.
- 7. (A) For drying ammonia gas, the common dehydrating agents like H<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub> or P<sub>2</sub>O<sub>5</sub> cannot be used.
  - (R) H<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub> or P<sub>2</sub>O<sub>5</sub> react with NH<sub>3</sub>.
- 8. (A) Phosphorite mineral cannot be used as a fertilizer of phosphorus.
  - (R) Superphosphate of lime is used as a fertilizer of phosphorus.
- 9. (A) H<sub>3</sub>PO<sub>3</sub> is a dibasic acid.
  - (R) There are two H-atoms directly attached to P.

[A.I.I.M.S. 2007]

## Auswers

**1.** (c)

**2.** (a)

**3.** (b)

4. (c)

and the second of the contract

5. (d)

**6.** (e)

7. (a)

**8.** (b)

9. (c)

# THOUGHT TYPE QUESTIONS

#### THOUGHT 1

Nitrogen, phosphorus and potassium are regarded as essential plant nutrients. After a few years of continuous cultivation, the soil becomes poorer and poorer in materials supplying nitrogen, phosphorus and potassium to plants. If the soil is not compensated, it would become less productive and infertile. In order to maintain soil fertility, it is necessary to add materials containing nitrogen, phosphorus and potassium in the form of fertilizers. Chemical substances which are added to the soil as to make up the deficiency of essential elements are called chemical fertilizers. Every chemical compound of nitrogen, phosphorus and potassium cannot be used as a fertilizer. Substances to be used as fertilizers must have the following characteristics:

- (a) it must be soluble in water
- (b) it should be easily assimilated by plants
- (c) it should be stable
- (d) it should not disturb the pH of the soil
- (e) it should be cheap

The important nitrogeneous fertilizers are:

- (a) ammonium sulphate
- (b) calcium cyanamide

- (c) calcium ammonium nitrate
- (d) urea
- (e) basic calcium nitrate

The important phosphatic fertilizers are:

- (a) calcium superphosphate
- (b) nitrophosphate
- (c) triple phosphate
- (d) phosphatic slag

The commonly used potassium fertilizers are:

- (a) potassium nitrate
- (b) potassium chloride
- (c) potassium sulphate

Fertilizers containing N, P and K in suitable adjusted proportions are known as NPK fertilizers.

- 1. Which one of the following substances is used as a fertilizer?
  - (a)  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
  - (b) Ca(CN)<sub>2</sub>
  - (c)  $Ca(H_2PO_4)_2H_2O\cdot 2(CaSO_4\cdot 2H_2O)$
  - (d) CaSO<sub>4</sub>
- 2. Fertilizer having highest percentage of nitrogen is :
  - (a) urea

- (b) calcium cyanamide
- (c) ammonium nitrate
- (d) ammonium sulphate

Elen	nents of Group VA or 15 (E	lements of Nitrogen and Phosp
3.	Sindhri fertilizer is chemical	lv known as :
	(a) ammonium nitrate	(b) ammonium sulphate
	(c) urea	(d) calcium nitrate
4.	Ammonium salts are oxidise	
	(a) denitrifying bacteria	(b) ammonifying bacteria
	(c) nitrosifying bacteria	
5.	The actual composition of n	itrolim is :
	(a) Ca(CN) <sub>2</sub>	(b) $CaC_2 + Ca(CN)_2$
	(c) CaCN <sub>2</sub> +C	(d) CaH <sub>2</sub>
6.	Expression like 4-8-2 used	for a NPK mixed fertilizer indi-
	cates that it contains:	
	(a) 4% N <sub>2</sub> , 8% P <sub>2</sub> O <sub>5</sub> and 2%	6 K <sub>2</sub> O
	(b) 4% urea, 8% Ca(H <sub>2</sub> PO <sub>4</sub> )	<sub>2</sub> and 2% KCl
	(c) 4% NH <sub>3</sub> , 8% H <sub>3</sub> PO <sub>4</sub> and	2% K <sub>2</sub> SO <sub>4</sub>
	(d) 4% NH <sub>4</sub> NO <sub>3</sub> , 8% P <sub>2</sub> O <sub>5</sub> a	and 2% KNO <sub>3</sub>
ΙH	OUGHT 2	
Γ	The pronounced change from n	on-metallic to metallic behaviour
		oxides from nitrogen to bismuth
		ncreasing size of the atoms. The
		very high on account of its small
size	. However, ionisation potentia	al decreases regularly on descen-
ding	g the group.	
1.	Which one of the following	g is a strongest base ?
	(a) AsH <sub>3</sub>	(b) SbH <sub>3</sub>
	(c) PH <sub>3</sub>	(d) NH <sub>3</sub>
2.	Among the trihalides of nitr	ogen, which one is least basic?
	(a) $NF_3$	(b) NCl <sub>3</sub>
	(c) NBr <sub>3</sub>	(d) NI <sub>3</sub>
3.	Which one of the following	fluorides does not exist?
	(a) NF <sub>5</sub>	(b) PF <sub>5</sub>
	(c) AsF <sub>5</sub>	(d) SbF <sub>5</sub>
4.	Which of the following oxi	des is most acidic?
	(a) $Bi_2O_3$	(b) P <sub>2</sub> O <sub>3</sub>
	(c) $As_2O_3$	(d) $Sb_2O_3$
5.	The most unstable hydride	
	(a) NH <sub>3</sub>	(b) PH <sub>3</sub>
	(c) BiH <sub>3</sub>	(d) SbH <sub>3</sub>
6.		nents, the number of unpaired
	electrons in the valence she	
	(a) 4	(b) 3

· (d) 5

(b) PCl<sub>3</sub>

(d) SbF<sub>3</sub>

7. Which trihalide is most ionic among the following?

THOUGHT 3

structures and oxidation state of phosphorus. All the acids contain

phosphorus atom/atoms linked tetrahedrally to four other atoms

or groups. Each of them has at least one P=O or  $P\to O$  unit and one P-OH unit. The OH group is ionisable but H atom linked

directly to P is non-ionisable. Structures of all the acids are considered to be derived either from phosphorus acid or

Phosphorus forms a number of oxoacids which differ in their

(c) 2

(a) NCl<sub>3</sub>

(c) BiF<sub>3</sub>

phosphoric acid.

1	Which	one	:	monobasic	00:42	
ı.	wnich	one	18	monobasic	acia?	

- (a)  $H_3PO_2$
- (b) H<sub>3</sub>PO<sub>3</sub>
- (c) H<sub>3</sub>PO<sub>4</sub>
- (d) H<sub>3</sub>PO<sub>5</sub>

#### Which one has +4 oxidation state?

- (a) H<sub>3</sub>PO<sub>4</sub>
- (b) H<sub>3</sub>PO<sub>3</sub>
- (c)  $H_4P_2O_7$
- (d)  $H_4P_2O_6$
- 3. The acid which forms two series of salts is:
  - (a) H<sub>2</sub>PO<sub>4</sub>
- (b) H<sub>3</sub>PO<sub>3</sub>
- (c) H<sub>3</sub>BO<sub>3</sub>
- (d) H<sub>3</sub>PO<sub>2</sub>
- Which of the following is a cyclic oxoacid?
  - (a)  $H_4P_2O_7$
- (b)  $H_4P_2O_6$
- (c) H<sub>3</sub>P<sub>3</sub>O<sub>9</sub>
- (d)  $H_5P_5O_{15}$
- 5. The number of  $P \rightarrow O$  or P = O and  $P \rightarrow O \rightarrow H$  bonds in H<sub>3</sub>PO<sub>4</sub> are:
  - (a) 3, 1

(b) 2, 2

(c) 1; 2

(d) 1, 3

#### THOUGHT 4

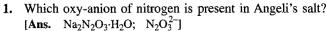
There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH<sub>3</sub> and PH<sub>3</sub>. PH<sub>3</sub> is a flammable gas and is prepared from white phosphorus. [I.I.T. 2008]

- 1. Among the following, the correct statement is:
  - (a) Phosphates have no biological significance in humans
  - (b) Between nitrates and phosphates, phosphates are less abundant in earth's crust
  - (c) Between nitrates and phosphates, nitrates are less abundant in earth's crust
  - (d) Oxidation of nitrates is possible in soil
- Among the following, the correct statement is:
  - (a) Between NH<sub>3</sub> and PH<sub>3</sub>, NH<sub>3</sub> is a better electron donor because the lone pair of electrons occupies spherical s-orbital and is less directional.
  - (b) Between NH3 and PH3, PH3 is a better electron donor because the lone pair of electrons occupies sp<sup>3</sup>-orbital and is more directional.
  - (c) Between NH<sub>3</sub> and PH<sub>3</sub>, NH<sub>3</sub> is a better electron donor because the lone pair of electrons occupies  $sp^3$ -orbital and is more directional.
  - (d) Between NH3 and PH3, PH3 is a better electron donor because the lone pair of electrons occupies spherical s-orbital and is less directional.
- White phosphorus on reaction with NaOH gives PH<sub>3</sub> as one of the products. This is a:
  - (a) dimerization reaction
  - (b) disproportionation reaction
  - (c) condensation reaction
  - (d) precipitation reaction
  - [Hint:  $P_4^0 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$ ]

## Auswers

	كالمحاج						
Thought 1	1. (c)	<b>2.</b> (a)	<b>3.</b> (b)	<b>4.</b> (d)	<b>5.</b> (c)	<b>6.</b> (a)	
Thought 2	<b>1.</b> (d)	<b>2.</b> (a)	3. (a)	<b>4.</b> (b)	<b>5.</b> (c)	<b>6.</b> (b)	<b>7.</b> (c)
Thought 3	1. (a)	<b>2.</b> (b)	<b>3.</b> (b)	<b>4.</b> (c)	<b>5.</b> (d)		
Thought 4	1 (c)	2. (c)	3. (b)				

## BRAIN STORMING PROBLEMS



- Write down the two compounds of Vth or 15th group elements which are covalent in vapour state but ionic in solid state. [Ans.  $N_2O_5$ ,  $PCl_5$ ]
- Write the formula of:
  - (i) Scheele's green
- (iii) Graham salt
- (ii) Paris green
- (iv) Pearl white
- (i) CuHAsO3;
- (ii) (CH<sub>3</sub>COO)<sub>2</sub>Cu.3Cu(AsO<sub>2</sub>)<sub>2</sub>
- (iii) (NaPO<sub>3</sub>)<sub>6</sub>;
- (iv) BiOCl]
- Explain why all P—F bonds in PF<sub>5</sub> are not equivalent? [Ans. Phosphorus in PF<sub>5</sub> lie in  $sp^3d$  hybrid state, out of five P-F bonds, three are equatorial bonds which have different length.]
- 5. Write comment on non-existance of PI<sub>5</sub>?
- Although phosphorus pentabromide exists in the vapour phase as PBr<sub>5</sub> molecules, in the solid phase the substance is ionic and has the structure [PBr<sub>4</sub>] +Br. What is the expected geometry of PBr<sub>4</sub><sup>+</sup>?

[Ans. Tetrahedral]

7. With the help of NH<sub>3</sub>, O<sub>2</sub>, Pt and H<sub>2</sub>O, write equations for preparation of N<sub>2</sub>O from these substances.

[Hint: 
$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt} 4NO(g) + 6H_2O(g)$$
  
 $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$   
 $3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq.) + NO(g)$   
 $HNO_3(g) + NH_3(aq.) \longrightarrow NH_4NO_3(aq.)$   
 $NH_4NO_3(aq.) \xrightarrow{\Delta} NH_4NO_3(s)$   
 $NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(g)$ ]

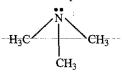
- 8. Give the formula of:
  - (i) Polyphosphoric acid
  - (ii) Polymetaphosphoric acid
  - (iii) Sodium triphosphate
  - (iv) Trimetaphosphate

Ans.

- (i)  $H_{n+2} P_n O_{3n+1}$ ;
- (ii)  $(HPO_3)_n$ ;
- (iii) Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub> ;
- (iv) Na<sub>3</sub>P<sub>3</sub>O<sub>9</sub>]
- 9. Write down the formula of those compounds of phosphorus which are used as:
  - (i) detergent additive
- (ii) in soft drink
- (iii) in tooth powder
- (iv) animal feed additive

- [Ans.
- (i) Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>;
- (ii) H<sub>3</sub>PO<sub>4</sub>;
- (iii) CaHPO<sub>4</sub>·2H<sub>2</sub>O;
- (iv) CaHPO<sub>4</sub>·2H<sub>2</sub>O]
- 10. Comment on the structure of trimethyl amine [(CH<sub>3</sub>)<sub>3</sub>N] and trisilyl amine [(SiH<sub>3</sub>)<sub>3</sub>N].

[Hint: Trimethyl amine has pyramidal structure like NH3 because lone pair of electron is present at nitrogen.



Trisilyl amine has planar structure because lone pair of nitrogen is donated to vacant d-orbital of silicon.]



- 11. Explain why NF<sub>3</sub> has no donor property of electrons but PF<sub>3</sub> has, and PF3 forms several complexes.
- What is composition of Devarda's alloy? Which gas is evolved when this alloy is treated with HNO3? [Ans. Al 45%; Zn 5%; Cu 50%; NH<sub>3</sub>(g)]
- 13. When HNO<sub>3</sub> is added to conc. H<sub>2</sub>SO<sub>4</sub> we get NO<sub>2</sub><sup>+</sup> and  $NO_3^-$ ; explain this fact.

[Hint: 2HNO<sub>3</sub> 
$$\xrightarrow{\text{Conc. H}_2\text{SO}_4}$$
  $N_2\text{O}_5$  +  $H_2\text{O}_5$ 

In polar solvent, N<sub>2</sub>O<sub>5</sub> gives solvated ions NO<sub>2</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>.]

14. Explain why nitride of lithium (Li<sub>3</sub>N) is more stable than nitride of potassium (K<sub>3</sub>N)?

[Hint: Lattice energy of Li<sub>3</sub>N is very high.]

15. In oxidation of  $P_4$  to  $P_4O_6$  we cannot use pure  $O_3$ ; we use mixture of O<sub>3</sub> and N<sub>2</sub>. What is the reason behind it?

[Hint: Pure O<sub>2</sub> will oxidise P<sub>4</sub>O<sub>6</sub> to P<sub>4</sub>O<sub>10</sub>.]

- 16. Arrange the following as indicated:
  - (a) As<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>3</sub> (Decreasing acid strength)
  - (b) P<sub>2</sub>O<sub>5</sub>, N<sub>2</sub>O<sub>5</sub>, As<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>5</sub>, Sb<sub>2</sub>O<sub>5</sub>

(Decreasing acid strength)

- (c) N<sub>2</sub>O<sub>5</sub>, N<sub>2</sub>O<sub>5</sub>, N<sub>2</sub>O<sub>4</sub>, N<sub>2</sub>O<sub>3</sub>, NO (Increasing acid strength)
- (d) P<sub>2</sub>O<sub>5</sub>, Bi<sub>2</sub>O<sub>5</sub>, N<sub>2</sub>O<sub>5</sub>, Sb<sub>2</sub>O<sub>5</sub>, As<sub>2</sub>O<sub>3</sub> (Decreasing stability)
- (e) NBr<sub>3</sub>, NCl<sub>3</sub>, NF<sub>3</sub> (Decreasing stability)
- (f) NI<sub>3</sub>, NBr<sub>3</sub>, NCl<sub>3</sub>, NF<sub>3</sub> (Increasing Lewis base strength)
- (g) BiCl<sub>3</sub>, NCl<sub>3</sub>, PCl<sub>3</sub>, AsCl<sub>3</sub>, SbCl<sub>3</sub>

(Decreasing trend of hydrolysis)

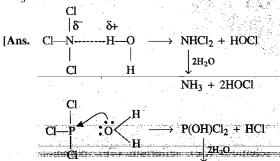
- (h) PF<sub>3</sub>, PCl<sub>3</sub>, PBr<sub>3</sub>, PI<sub>3</sub> (Decreasing Lewis acid strength)
- (i) H<sub>3</sub>SbO<sub>4</sub>, H<sub>3</sub>AsO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub>

(Decreasing solubility in water)

[Ans. (a)  $N_2O_3 > P_2O_3 > As_2O_3$ 

(b)  $N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5 > Bi_2O_5$ 

- (c)  $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$
- (d)  $P_2O_5 > As_2O_3 > Sb_2O_5 > N_2O_5 > Bi_2O_5$
- (e)  $NF_3 > NCl_3 > NBr_3$
- (f)  $NF_3 < NCl_3 < NBr_3 < NI_3$
- (g)  $NCl_3 > PCl_3 > AsCl_3 > SbCl_3 > BiCl_3$
- (h)  $PF_3 > PCl_3 > PBr_3 > PI_3$
- (i)  $HNO_3 > H_3PO_4 > H_3AsO_4 > H_3SbO_4$ .]
- 17. What are the products formed by hydrolysis of NCl<sub>3</sub> and PCl<sub>3</sub>?



$$H_3PO_3 + 2HCl$$

- **18.** NF<sub>3</sub> is stable but NCl<sub>3</sub> and NI<sub>3</sub>, are unstable and explosive. Explain why?
  - **[Hint:** In NF<sub>3</sub>, there is strong  $p\pi$ - $p\pi$  bonding due to large electronegativity difference between N(3) and F(4). On the other hand, there, is weak  $p\pi$ - $p\pi$  bonding in NCl<sub>3</sub> and NI<sub>3</sub>, hence these compounds are unstable and explosive.]
- 19. Complete the following reactions:
  - (a)  $[Fe(CO)_5] + NO \longrightarrow$
  - (b)  $KNO_3 + KNO_2 + Cr_2O_3 \longrightarrow$
  - (c)  $Cr^{2+} + H^{+} + NO \longrightarrow$
  - (d)  $SO_2 + NO + H^+ \longrightarrow$
  - (e)  $MnO_4^- + NO + H^+ \longrightarrow$

- (f)  $SO_3^{2-} + NO_2^{-} + H^+ \longrightarrow$
- [Ans. (a)  $[Fe(CO)_5] + 2NO \xrightarrow{\Delta} [Fe(CO)_2(NO)_2] + 3CO$
- (b)  $3KNO_2 + KNO_3 + Cr_2O_3 \xrightarrow{\Delta} 2K_2CrO_4 + 4NO$
- (c)  $3Cr^{2+} + NO + 3H^{+} \longrightarrow NH_2OH + 3Cr^{3+}$
- (d)  $SO_2 + 2NO + H_2O \longrightarrow N_2O + H_2SO_4$
- (e)  $3MnO_4^- + 5NO + 4H^+ \longrightarrow 5NO_3^- + 3Mn^{2+} + 2H_2O$
- (f)  $SO_3^{2-} + 2NO_2^- + 2H^+ \longrightarrow SO_4^{2-} + 2NO_1^- + H_2O_1^-$
- 20. Answer the following questions:
  - (a) What is Swart's reagent?
  - (b) Give chemical formula of Vortex ring.
  - (c) Cold fire and Phossy Jaw are related to.....
  - (d) Which gas of nitrogen is used as anaesthetic in dental surgery?
  - (e) Give the chemical formula of phosphorus sulphide present in 'strike anywhere matches'.
  - (f) What is 'Ghost light'?
  - (g) What is the chemistry of Holme's signal?
  - [Ans. (a) SbF<sub>3</sub> is a fluorinating agent called Swart's reagent.
    - (b) White smokes of P<sub>2</sub>O<sub>5</sub> is called Vortex ring.
    - (c) White phosphorus.
    - (d) N<sub>2</sub>O
    - (e) P<sub>4</sub>S<sub>3</sub>
    - (f) Bones glow in dark due to oxidation of white phosphorus present. The phenomenon is called chemiluminescence.
    - (g) Mixture of CaC<sub>2</sub> and Ca<sub>3</sub>P<sub>2</sub> filled in container with a hole is thrown into sea or river, so that following reactions take place:

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3 \text{ or } P_2H_4$$

P<sub>2</sub>H<sub>4</sub>, catches fire. The acetylene produces a bright luminous flame which serves as a signal to approaching ship or boat (Holme's signal).]

## INTEGER ANSWER Tupe Outstions

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. How many nitrogen oxides are known?
- 2. How many lone pairs are present in nitrogen molecule?
- 3. In group 15 elements, the number of unpaired electrons in valence shell is:
- 4. How many P—O—P bonds are present in P<sub>4</sub>O<sub>8</sub>?
- 5. When excess of ammonia and chlorine react, nitrogen and ammonium chloride are formed. Write the balanced equation and find out how many ammonium chloride molecules are involved in the balanced equation?
- 6. How many  $\sigma$ -bonds are present in  $N_2O_3$ ?
- 7. What is the basicity of pyrophosphoric acid?
- **8.** In solid PCl<sub>5</sub> molecule, how many P—Cl bonds are present in the cation?

### Answers

- 1. (5) Five oxides are known. These are  $N_2O$ , NO,  $N_2O_3$ , NO<sub>2</sub> and  $N_2O_5$ .
- 2. (2) Nitrogen molecule has a triple bond and each nitrogen atom is associated with a lone pair of electrons. :N == N:
- 3. (3) The valence shell in group 15 elements is  $ns^2np^3$  i.e., all the three p-orbitals are occupied by single electron each.
- 4. (6) The structure of  $P_4O_8$  is :  $O \leftarrow P \xrightarrow{O} O \xrightarrow{P} O P \rightarrow O$
- 5. (6)  $2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl$   $6NH_3 + 6HCl \longrightarrow 6NH_4Cl$   $8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$
- **6.** (4) The structure of  $N_2O_3$  is  $O^1 = N^2 O^3 N^4 = O$
- 7. (4)  $H_4P_2O_7$ . It has four OH groups.
- 8. (4) [PCl<sub>4</sub>]<sup>+</sup>[PCl<sub>6</sub>]<sup>-</sup>

#### Group 16 or VIA 8 0 Oxygen 2s<sup>2</sup>2p<sup>4</sup> 16 S Sulphur 3s23p4 34 Se 4524p4 52 Te 5s<sup>2</sup>5p<sup>4</sup> Po 6s26p4 116 Uuh $7s^27p^4$

# CHAPTER

## Elements of Group VIA or 16

(The Oxygen Family,  $ns^2np^4$ )

#### Contents:

11.1 Position in Periodic Table

11.2 Abnormal Behaviour of Oxygen

11.3 Dissimilarities between Oxygen and Sulphur

11.4 Oxygen

11.5 Oxides

11.6 Ozone

11.7 Sulphur

11.8 Compounds of Sulphur

Group Period	VA (15)	VIA (16)	VIIA (17)
. 2	N (7)	O (8)	F (9)
3	P (15)	S (16)	Cl (17)
4	As (33)	Se (34)	Br (35)
5	Sb (51)	Te (52)	I (53)
6	Bi (83)	Po (84)	At (85)
. 7	Uup (115)	Uuh (116)	

#### 11.1 POSITION IN PERIODIC TABLE

Group 16 or VIA of the extended form of periodic table consists of six elements—oxygen (O), sulphur (S), selenium (Se), tellurium (Te), polonium (Po) and ununhexium (Uuh)\*. This family is known as oxygen family. These (except polonium and ununhexium) are the ore forming elements and thus called **chalcogens.** These are *p*-block elements as the last differentiating electron is accommodated on *np* shell. These elements have six electrons in their valency shell and thus placed in the VIth group.

The elements oxygen and sulphur are common while selenium, tellurium and polonium are comparatively rare. Oxygen is the most abundant element and is found both in free as well as in combined state. Oxygen makes up 20.9% by volume and 23% by mass of atmosphere. Most of the oxygen present in the atmosphere is produced by photosynthesis in plants. It also occurs in the form of ozone in the upper atmosphere which protects us from the harmful radiations of the sun. Oxygen makes up 46.6% by mass of the earth's crust. Sulphur is the sixteenth most abundant element and constitutes 0.034% by mass of the earth's crust. It occurs mainly in combined form. The member, polonium is radioactive in nature. The inclusion of these elements in the same subgroup is justified on the basis of same electronic configuration and similarities as well as gradation in their physical and chemical properties.

Like other groups, the first element oxygen differs from other elements of the group in several respects.

#### 3 1. Electronic Configuration

The distribution of electrons in various energy shells of the atoms of these elements is given as below:

Element	At. No.	-	With inert gas core	
Oxygen	8	2, 6	$1s^2$ , $2s^2$ $2p^4$	[He] $2s^2 2p^4$
Sulphur	16	2, 8, 6	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^4$	[Ne] $3s^2 3p^4$
Selenium	34	2, 8, 18, 6	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^4$	[Ar] $3d^{10}$ , $4s^2 4p^4$
Tellurium	52	2, 8, 18, 18, 6	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ , $5s^2$ $5p^4$	[Kr] $4d^{10}$ , $5s^2$ $5p^4$
Polonium	84	2, 8, 18, 32, 18, 6	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ , $5s^2$ $5p^6$ $5d^{10}$ , $6s^2$ $6p^4$	[Xe] $4f^{14}$ , $5d^{10}$ , $6s^2$ $6p^4$
Ununhexium	116	2, 8, 18, 32, 32, 18, 6	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ , $5s^2$ $5p^6$ $5d^{10}$ $5f^{14}$ ,	[Rn] $5f^{14}$ , $6d^{10}$ , $7s^2$ $7p^4$
		. `	$6s^2 6p^6 6d^{10}, 7s^2 7p^4$	

<sup>\*</sup>Recently a new element with atomic number 116 (Ununhexium) has been discovered. It is a synthetic and radioactive element. It is not very stable element. Not much is known about its properties.

All have six electrons in their outermost shell, *i.e.*, they have electronic structure  $s^2p^4$ . The penultimate shell contains 2 electrons in oxygen, 8 electrons in sulphur and 18 electrons in Se, Te, Po and Uuh. This explains why oxygen differs from sulphur and these two from the remaining elements.

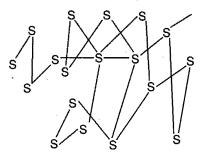
#### 2. Physical Characteristics

(a) Physical state: Oxygen is a gas while others are solids. Oxygen molecule is diatomic while the molecules of other elements are more complex. Sulphur, selenium and tellurium exist as staggered 8-atom rings. However, the tendency to exist in 8-atom rings is maximum with sulphur and decreases as we go down the group. In  $S_8$  molecule, every sulphur atom is in  $sp^3$  hybridized state involving both bonding and non-bonding pairs of electrons.

Fig. 11.1 Staggered ring structure of sulphur molecule, S<sub>8</sub>

[Oxygen atom has the tendency to form multiple bonds ( $p\pi$ — $p\pi$  interaction) with other oxygen atom on account of small size while this tendency is missing in sulphur atom. The bond energy of oxygen-oxygen double bond (O=O) is quite large (about three times that of oxygen-oxygen single bond, O—O = 34.9 kcal mol<sup>-1</sup>) while sulphur-sulphur double bond (S=S) is not so large (less than double of sulphur-sulphur single bond, S—S = 63.8 kcal mol<sup>-1</sup>). As a result, —O—O—O— chains are less stable as compared to O=O molecule while —S—S—S— chains are more stable than S=S molecule. Therefore, at room temperature, while oxygen exists as a diatomic gas molecule, sulphur exists as S<sub>8</sub> solid.]

The plastic sulphur which is formed by pouring liquid sulphur into water contains zig-zag long chains of sulphur atoms.



At temperatures above the boiling points, sulphur forms a red vapour, which turns to yellow as temperature is increased. In vapour there exist  $S_8$ ,  $S_6$  and  $S_2$  molecules. Above 1000°C, there exist only  $S_2$  molecule, which has structure like  $O_2$ .

(b) Metallic and non-metallic character: Metallic character increases with the increase of atomic number. Oxygen

and sulphur are distinctly non-metallic. Selenium and tellurium show both non-metallic and metallic characters but polonium is definitely a metal.

- (c) There is a gradual gradation in physical properties:
- (i) Atomic and ionic radii: The atomic radii of the elements of group 16 are smaller than those of the corresponding elements of group 15. The atomic radii of the elements of this group increase gradually on moving down the group.

The smaller atomic radii of group 16 elements as compared with corresponding elements of groups 15 are due to the increased effective nuclear charge with increase in greater attraction towards nucleus. The attraction brings contraction in size. The gradual increase on moving down the group is due to the increase in the number of electron shells from member to member.

In the formation of anions, two electrons are being added to an atom. Therefore, the effective nuclear charge is reduced and hence, the electron closed expands. Thus, the negative ions  $(M^2)$  are bigger in size than the corresponding atoms. Like atomic radii, ionic radii also increase gradually on moving down the group.

(ii) Ionisation energy: The ionisation enthalpies are high and thus the elements do not lose the electrons to form positive ions easily. The values decrease as the atomic number increases from O to Po and thus the tendency to form positive ion increases gradually, *i.e.*, metallic nature increases.

	О	S	Se	Te	Po
Ionisation energy $\Delta_i H_1$ (kJ mol <sup>-1</sup> )	1314	1000	941	869	813
,	3388	2251	2045	1790	· –

The ionisation energies of first three elements of group 16 are less than corresponding elements of group 15 inspite of the fact that nuclear charge increases. The abnormal behaviour is due to symmetrical and more stable electronic configuration of N, P and As as compared to O, S and Se respectively.

Decreases gradually

However, the second ionisation values of group 16 elements are higher than those of group 15.

(iii) Electronegativity: Electronegativity decreases gradually. Oxygen is second most electronegative element after fluorine.

This decrease indicates a change from non-metallic to metallic character.

(iv) Melting and boiling points: The melting and boiling points increase gradually with increase in atomic number.

O S Se Te

Melting point (°C) -219 119 217 450

(Monoclinic)

Boiling point (°C) -183 445 688 990

(v) Electron affinity: Group 16 elements have high electron affinities. On moving from oxygen to sulphur, the  $EA_1$  value increases and then decreases from S to Po:

Element O S Se Te Po  $EA_1 (kJ mol^{-1})$  -141 -200 -195 -190 -183

The electron density in 2p energy shell in oxygen is high due to small size of oxygen atom and thus, there is some resistance to the incoming electron and thereby the  $EA_1$  of oxygen is comparatively low. Sulphur has maximum value and on moving from S to Po, the  $EA_1$  values decrease due to increased size.

(d) Allotropy: All the elements show allotropy:

 Element
 Allotropic forms

 Oxygen
 Ordinary oxygen and ozone

 Sulphur
 Rhombic, monoclinic, plastic, amorphous

 Selenium
 Red form (non-metallic), grey form (metallic form)

 Tellurium
 Crystalline and amorphous

 Polonium
 α and β forms (Both are metallic forms)

(e) Catenation: Oxygen and sulphur show the property of catenation. The property is more pronounced in sulphur. H—O—O—H, H—S—S—H, H—S—S—H, H—S—S—H, H—S—S—H, the peroxides and polysulphides are fairly stable.

Note: Catenated compounds of sulphur are the following:

- (i) Polysulphides:  $S_n^{2-}$  where n = 2, 3, 4, etc.
- (ii) Sulphanes: X—S<sub>n</sub>—X, where X = I, Cl, CN, etc. Compounds corresponding to n ~ 100 have been reported.
- (iii) Polysulphonic acids: These have general formula HO<sub>3</sub>S—S<sub>n</sub>—SO<sub>3</sub>H compounds corresponding to n ~ 22 have been reported. These are also called thionic acids.
- (f) Oxidation states: As the configuration of outermost shell is  $ns^2$   $np^4$ , these elements try to gain or share two electrons in order to attain inert gas configuration. Oxygen being highly electronegative shows -2 oxidation state in its compounds except in oxygen fluorides and most of the metal oxides are ionic and contain oxygen as dinegative anion,  $O^{2-}$ . Since, the electronegativity decreases, the tendency to exhibit -2 oxidation state decreases as we go down in the group. However, positive oxidation states are exhibited by S, Se, Te and Po. In addition to +2 oxidation state, +4 and +6 oxidation states are observed. This is due to the availability of d-orbitals in these elements. Oxygen has no d-orbitals and hence cannot show +4 and +6 oxidation states while sulphur can have 2, 4 or 6 unpaired orbitals forming 2, 4 or 6 covalent bonds.

S-atom	3 <i>s</i>	3 <i>p</i>		
(Ground state)	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\uparrow$		+2
S-atom (Excited state)	$\uparrow\downarrow$	$\uparrow \uparrow \uparrow \uparrow$	$\uparrow$	+4
S-atom (Doubly excited state)	$\uparrow$	$\boxed{\uparrow   \uparrow   \uparrow}$	$\uparrow$	+6

Thus, oxygen is never more than divalent while other members may be divalent, tetravalent and hexavalent. The compounds having +4 oxidation state show both oxidising and reducing properties while compounds having +6 oxidation states are only oxidising.

(g) Multiple bonding: Oxygen atom has the tendency to form multiple bonds ( $p\pi$ – $p\pi$  interaction) with the other oxygen atom on account of small size and high electronegativity. However, the rest of the elements do not form  $p\pi$ – $p\pi$  multiple bonds due to their large size. Sulphur and higher members of group 16 possess vacant d-orbitals in their valence shell. They use these orbitals to form  $d\pi$ – $p\pi$  bonds. However, this tendency is maximum and stronger in sulphur and decreases from sulphur onwards.

#### 3. Trends in Chemical Reactivity

Oxygen is the most reactive element of the group despite it has high bond dissociation energy of oxygen molecule (493.4 kJ mol<sup>-1</sup>) as nearly all its reactions are exothermic. Once initiated, these reactions continue spontaneously. Oxygen directly combines with almost all the metals except noble metals, all the non-metals except noble gases and halogens and many compounds under suitable conditions. The oxides are generally stable compounds. The elements such as W, Pt, Au, halogens and noble gases which do not directly combine with oxygen, form compounds with oxygen indirectly.

After oxygen, sulphur is quite reactive element especially at high temperatures which help in breaking of S—S bonds. Sulphur burns in air and reacts directly with carbon, phosphorus, arsenic and many metals. Oxidising acids oxidise it into  $SO_2$  and alkalies dissolve it to give sulphides and thiosulphates. It reacts with  $H_2$  and halogens. The sulphides are stable compounds and many metals are found in nature in the form of sulphides.

However, the reactivity of group 16 elements decreases from oxygen to polonium.

Selenium and tellurium combine with highly electropositive elements such as alkali and alkaline earth metals. Se and Te combine with oxygen, fluorine and chlorine. In general, the compounds of selenium and tellurium are less stable than oxygen and sulphur.

Some important trends in chemical reactivity of elements of group 16 are discussed here.

#### (a) Hydrides

All the elements of this group form the hydrides of type  $H_2M$  where, M = O, S, Se, Te and Po, *i.e.*,

 $H_2O$  is obtained by burning hydrogen in the atmosphere of oxygen while  $H_2S$ ,  $H_2Se$  and  $H_2Te$  are obtained by the action of acids on sulphides, selenides and tellurides.

FeS + 
$$H_2SO_4 \longrightarrow FeSO_4 + H_2S$$
  
Na<sub>2</sub>Se +  $H_2SO_4 \longrightarrow Na_2SO_4 + H_2Se$ 

(i) Physical state: Water is colourless, odourless liquid while other hydrides are colourless, poisonous gases with bad odours.

- (ii) Volatility: Water has low volatility (high boiling point) as hydrogen bonding brings association.  $H_2S$  has high volatility as no hydrogen bonding is present. Volatility decreases from  $H_2S$  to  $H_2$ Te due to increase in molecular masses of the hydrides.
- (iii) Covalent character: As the electronegativity difference between M and H decreases, the covalent character of these hydrides increases from  $H_2O$  to  $H_2Te$ . Water molecule is highly polar. It has high dielectric constant and hence acts as an excellent solvent for inorganic compounds.
- (iv) Thermal stability: The thermal stability decreases as the atomic mass increases. Water dissociates at  $2000^{\circ}$ C while tellurium hydride,  $H_2$ Te, decomposes at room temperature. This is due to an increase in M—H bond length.
- (v) Acidic nature: The hydrides are all weak acids and dissociate to varying degrees to give  $H^+$  ions. The acidic strength increases from  $H_2O$  to  $H_2Te$  as it is evident from the values of dissociation constants.

$$H_2O$$
  $H_2S$   $H_2Se$   $H_2Te$  Dissociation  $1.0 \times 10^{-14}$   $1.0 \times 10^{-7}$   $1.7 \times 10^{-4}$   $2.3 \times 10^{-3}$  constant (25°C)

The increasing trend can be explained on the basis of dissociation energies. The dissociation energies decrease as the bond length M—H increases from oxygen to tellurium. This facilitates the release of proton. The acidic nature can also be explained on the basis of charge density on  $M^{2-}$  anion. The charge density on the  $M^{2-}$  ion decreases as the size of M-atom increases from oxygen to tellurium. The decrease in charge density is responsible for the decrease in dissociation energies and thereby increasing the tendency to furnish proton.

- (vi) Reducing nature: All hydrides except  $H_2O$  act as reducing agents. The reducing nature increases as the atomic number of the central atom increases. This is due to weakening of M—H bond as the bond length increases with increase of size of M-atom.
- (vii) Burning:  $H_2S$ ,  $H_2Se$ ,  $H_2Te$  and  $H_2Po$  burn in atmosphere of oxygen with blue flame forming dioxides.

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2$$

(viii) Shape: All these hydrides are V-shaped. In these hydrides, the central atom is  $sp^3$ -hybridized. The bond angles are 104.5°, 92.5°, 91° and 90° in  $H_2O$ ,  $H_2S$ ,  $H_2Se$  and  $H_2Te$ , respectively.

This can be explained on the basis of decreasing electronegativity of central atom and decreasing tendency of  $sp^3$ -hybridization.

#### Other hydrides

Oxygen and sulphur have a tendency to form polyoxides and polysulphides which are comparatively less stable. The two common examples are  $H_2O_2$  (hydrogen peroxide) and  $H_2S_2$  (hydrogen disulphide). They decompose on heating.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$H_2S_2 \longrightarrow H_2S + S$$

Hydrogen polysulphides (H— $S_n$ —H', n may be 2, 3, 4, 5) are yellow oily liquids which possess a more strong odour than  $H_2S$ .

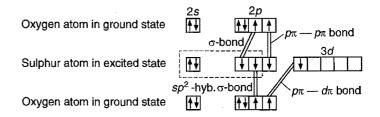
#### (b) Oxides

The most important oxides are of the type  $MO_2$  and  $MO_3$ .  $SO_2$  and  $SeO_2$  are acidic oxides and are soluble in water.  $TeO_2$  and  $PoO_2$  are insoluble in water. These are amphoteric oxides as they dissolve in both acids and bases.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$
 (Sulphurous acid)  
 $SeO_2 + H_2O \longrightarrow H_2SeO_3$  (Selenous acid)  
 $TeO_2 + 2NaOH \longrightarrow Na_2TeO_3 + H_2O$   
 $Sodium \ tellurite$   
 $2TeO_2 + HNO_3 \longrightarrow 2TeO_2 \cdot HNO_3 \ or \ Te_2O_3 \cdot (OH)NO_3$   
Basic nitrate

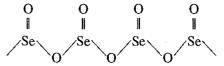
 $SO_2$  is a gas,  $SeO_2$  is a volatile solid and  $TeO_2$  is a white non-volatile solid. All the dioxides possess different structures.  $SO_2$  is an angular molecule with an O—S—O angle of 119.5°. The sulphur undergoes  $sp^2$ -hybridization. Both the bonds have same bond lengths. This suggests resonance in the molecule.

 $SeO_2$  has the same structure as  $SO_2$  in the gaseous state but the solid has a chain like structure which is not planar.



$$O_{p\pi} = \frac{\sigma}{p\pi} S_{p\pi} = \frac{\sigma}{d\pi} O \longrightarrow O_{p\pi} = \frac{\sigma}{d\pi} S_{p\pi} = \frac{\sigma}{d\pi} O \longrightarrow O_{p\pi} = \frac{\sigma}{d\pi} S_{p\pi} = \frac{\sigma}{d\pi} O$$

Fig. 11.2 Formation of SO<sub>2</sub> molecule



TeO<sub>2</sub> and PoO<sub>2</sub> are crystalline ionic solids.

**Trioxides:** SO<sub>3</sub>, SeO<sub>3</sub> and TeO<sub>3</sub> are acidic in nature.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$
 (Sulphuric acid)  
 $SeO_3 + H_2O \longrightarrow H_2SeO_4$  (Selenic acid)  
 $TeO_3 + 3H_2O \longrightarrow H_6TeO_6$  (Telluric acid)

The acidic nature decreases on moving down the group.  $SO_3$  is a gas and has plane triangular structure. The structure of  $SO_3$  is similar to that of  $SO_2$  except for the fact that lone pair of electrons of sulphur atom is donated to third oxygen atom. According to another view, the true structure of  $SO_3$  molecule is considered to be resonance hybrid of the following structures.

$$0 \longrightarrow 0 \longrightarrow 0 \longrightarrow 0 \longrightarrow 0$$

$$0 \longrightarrow 0 \longrightarrow 0 \longrightarrow 0$$

$$0 \longrightarrow 0 \longrightarrow 0$$

$$0 \longrightarrow 0 \longrightarrow 0$$

In the solid state, SO<sub>3</sub> exists as a cyclic trimer or a linear chain.

Cyclic trimer of SO<sub>3</sub>

Linear chain of SO<sub>3</sub>

Solid selenium trioxide is a cyclictetramer [Se<sub>4</sub>O<sub>12</sub>].

#### (c) Oxyacids or oxoacids

Sulphur forms a number of oxyacids but selenium and tellurium form only two series of oxyacids, the -ous and -ic acids.

$H_2SO_3$	$H_2SeO_3$	$H_2TeO_3$
Sulphurous acid	Selenous acid	Tellurous acid
Salts: Sulphite	Selenites	Tellurites
$H_2SO_4$	$H_2SeO_4$	H <sub>2</sub> TeO <sub>4</sub> or H <sub>6</sub> TeO <sub>6</sub>
Sulphuric acid	Selenic acid	Telluric acid
Sulphates	Selenates	Tellurates

Oxyacids with S—S linkages are called thioacids and with O—O linkages are termed peroxy acids. Thionic acids have two—SO<sub>3</sub>H groups linked either directly or through a S—chain (polythionic acids).

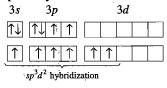
With increase oxidation number, the acid strength of oxyacid of an element increases, *i.e.*, sulphuric acid is stronger than sulphurous acid. In the oxyacids of group 16 elements in same oxidation state, the acidic nature decreases from S to Te. The -ous acids act as reducing agents while -ic acids act as oxidising

agents. These properties decrease from S to Te. Oxyacids are dibasic in nature.

#### (d) Halides

S, Se and Te form hexafluorides showing the maximum valency of six. They all involve  $sp^3d^2$  hybridization.

Sulphur atom in ground state
Sulphur atom in excited state



Thus, hexafluorides possess octahedral structure.

These are colourless gases. SF<sub>6</sub> is extremely inert.

Se $F_6$  is slightly reactive while Te $F_6$  is hydrolysed by water.

 $\text{TeF}_6 + 6\text{H}_2\text{O} \rightarrow 6\text{HF} + \text{H}_6\text{TeO}_6$ 

No other halogen forms the hexahalides due to larger size of Cl, Br and I.

Many tetrahalides are known. SF<sub>4</sub> is a gas, SeF<sub>4</sub> is a liquid while TeF<sub>4</sub> is a solid. S, Se, Te

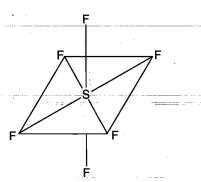
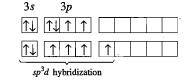


Fig. 11.3

and Po form tetrachlorides and bromides while Te and Po form tetraiodides. All tetrahalides possess trigonal bipyramid structure with  $sp^3d$  hybridization.

Sulphur atom in ground state Sulphur atom in excited state



Four unpaired electrons form bonds with four halogen atoms and one position is occupied by lone pair.

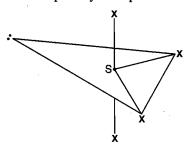
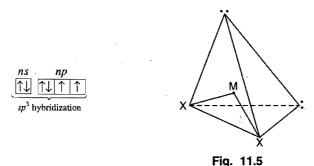


Fig. 11.4

 $SF_4$  is very reactive and is readily hydrolysed by water to give  $SO_2$  and HF inspite of the fact that average bond energy in  $SF_4$  is greater than  $SF_6$ . This is due to the presence of empty 3d-orbitals in sulphur atom in  $SF_4$ . It is used as fluorinating agent for many inorganic and organic compounds.

All the elements except selenium form stable dichlorides and dibromides. Di-iodides are not formed. Dihalides form tetrahedral molecules due to  $sp^3$  hybridization.



The bond angle is less than 109°28' due to the presence of lone pairs. The bond angle is 103° in SCl<sub>2</sub>, 101.5° in OF<sub>2</sub> and 98° in TeBr<sub>2</sub>.

Dimeric monohalides as  $S_2F_2$ ,  $S_2Cl_2$  and  $S_2Br_2$  are known. Their structure is similar to  $H_2O_2$ .

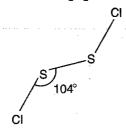


Fig. 11.6

[Note: As fluorine is more electronegative than oxygen, the compounds of oxygen and fluorine are called fluorides. For example, OF<sub>2</sub> is named oxygen difluoride. The compounds of oxygen and other halogens are called oxides as oxygen is more electronegative than chlorine, bromine and iodine. For example, ClO<sub>2</sub> is called chlorine dioxide and I<sub>2</sub>O<sub>5</sub> is named iodine pentoxide.]

#### (e) Oxyhalides

Only S and Se form oxyhalides. They are called thionyl and selenyl halides.

SOF <sub>2</sub>	· SOCl <sub>2</sub>	SOBr <sub>2</sub>
SeOF <sub>2</sub>	SeOCl <sub>2</sub>	SeOBr <sub>2</sub>

These react with water readily.

$$SOCl_2 + H_2O \longrightarrow SO_2 + 2HCl$$

In addition, sulphuryl halides are also known.

$$SO_2X_2$$

These may be regarded as derivatives of H<sub>2</sub>SO<sub>4</sub> where both the —OH groups have been replaced by two halogens atoms.

#### 11.2 ABNORMAL BEHAVIOUR OF OXYGEN

Oxygen differs from rest of the members of VIA group elements. The abnormal behaviour is attributed due to the following inherent characteristics:

- (i) Small size
- (ii) High electronegativity
- (iii) Non-availability of d-orbitals in the valency shell.

#### Points of difference

- (i) Oxygen is a gas while others are solids.
- (ii) It is diatomic molecule, while the rest are complex molecules, e.g.,  $S_8$ ,  $S_{e_8}$  with puckered ring structure.
- (iii) Oxygen is highly non-metallic due to high value of electronegativity.
- (iv) Oxygen is more ionic in its compounds. The dinegative anion  ${\rm O}^{2-}$  is quite common. The dinegative anions of other members are less common.
- (v) Oxygen exhibits an oxidation state of only -2 except in OF<sub>2</sub> and peroxides. It does not show +4 and +6 oxidation states as shown by other members.
- (vi) Oxygen molecule is highly stable. The two atoms are held together by multiple bonds. The bonds are fairly strong and bond energy is quite high (117 kcal per mole). It is only at a high temperature that these bonds are broken and oxygen atoms react with other materials. Thus, ordinary oxygen is not active under ordinary conditions.
- (vii) Hydrogen bonding is present in water and many other compounds due to high electronegativity of oxygen. On account of this, water boils at higher temperature.
- (viii) Oxygen molecule is paramagnetic in nature in gaseous, liquid and solid states. It is weakly attracted by a magnet. It has been explained by molecular orbital theory that oxygen molecule has two unpaired electrons.
  - (ix) Oxygen is the most abundant element in the earth's crust.
- (x) Metals like Cu, Ag, Hg, etc., show lesser affinity with O<sub>2</sub> to form oxide than with sulphur to form sulphide. It is due to polarizing power of Cu<sup>2+</sup>, Ag<sup>+</sup>, Hg<sup>2+</sup> ion, owing to which they form strong bond with S<sup>2-</sup>.

## 11.3 DISSIMILARITIES BETWEEN OXYGEN AND SULPHUR

Property	Oxygen	Sulphur
1. Electronic	2 electrons in the penul-	8 electrons in the penul-
configuration	timate orbit	timate orbit
2. Physical state	Colourless, odourless	Pale yellow solid with
	gas	faint odour
3. Abundance	Most abundant	Less abundant
4. Maximum covalency	2	6
5. Action of HNO <sub>3</sub>	Not affected	Oxidised to H <sub>2</sub> SO <sub>4</sub>
6. Nature of	H <sub>2</sub> O is neutral liquid	H <sub>2</sub> S is acidic gas under
hydride	under ordinary condi-	ordinary conditions. No
	tions. Hydrogen bond-	hydrogen bonding is
	ing is present.	present.
7. Molecule	Diatomic, O <sub>2</sub>	Octatomic, S <sub>8</sub>
8. Magnetic	Paramagnetic molecule	Diamagnetic molecule
nature		

#### 11.4 OXYGEN

**Historical:** Priestley and Schoole obtained oxygen within a few months of each other by heating suitable oxygen compounds. Schoole called it vital air or fire air. Lavoisier regarded it as an essential constituent of all acids and named it oxygen (oxus = acid, gennas = maker).

**Occurrence:** Oxygen occurs in the atmosphere to the extent of about 21% by volume (23% by mass). This percentage remains constant by the operation of the highly complex process termed **photosynthesis**. It is an essential ingredient in all living matter and is of great importance in respiration and combustion. It is most abundant element and forms about one half of the earth's crust. It forms a large part of nearly all the rocks and is present to the extent of 89% by weight in water.

#### **M** Preparation

Oxygen can be obtained in the laboratory by following methods:

(i) From oxides: (a) By thermal decomposition of the oxides of metals which are in lower part of electrochemical series.

$$2\text{HgO} \xrightarrow{450^{\circ}\text{C}} 2\text{Hg} + \text{O}_2; \quad 2\text{Ag}_2\text{O} \xrightarrow{350^{\circ}\text{C}} 4\text{Ag} + \text{O}_2$$

(b) By the thermal decomposition of higher oxides.

$$3MnO_2 \xrightarrow{\text{Heat}} Mn_3O_4 + O_2; \ 2Pb_3O_4 \xrightarrow{\text{Heat}} 6PbO + O_2$$

$$2BaO_2 \xrightarrow{\text{Heat}} 2BaO + O_2$$

- (c) By action of conc. H<sub>2</sub>SO<sub>4</sub> on MnO<sub>2</sub>.
  - $2MnO_2 + 2H_2SO_4 \longrightarrow 2MnSO_4 + 2H_2O + O_2$
- (d) By action of water on sodium peroxide (oxone).

$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$$

(ii) From salts: (a) Alkali nitrates on heating evolve oxygen.

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$
;  $2KNO_3 \longrightarrow 2KNO_2 + O_2$ 

(b) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KMnO<sub>4</sub> and KClO<sub>3</sub> decompose at high temperatures evolving oxygen.

$$4K_{2}Cr_{2}O_{7} \xrightarrow{400^{\circ}C} 4K_{2}CrO_{4} + 2Cr_{2}O_{3} + 3O_{2}$$

$$2KMnO_{4} \xrightarrow{250^{\circ}C} K_{2}MnO_{4} + MnO_{2} + O_{2}$$

$$2KClO_{3} \xrightarrow{400^{\circ}C} 2KCl + 3O_{2}$$

(c) By heating KMnO<sub>4</sub> or  $K_2Cr_2O_7$  with concentrated  $H_2SO_4$ .  $4KMnO_4 + 6H_2SO_4 \rightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$  $2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$ 

(d) By adding H<sub>2</sub>O<sub>2</sub> to acidified KMnO<sub>4</sub> solution.

$$2KMnO_4 + 3H_2SO_4(dil.) \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\frac{[H_2O_2 + O \rightarrow H_2O + O_2] \times 5}{2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2}$$

Pure oxygen is obtained by this reaction.

Laboratory preparation: The usual laboratory method consists in heating of a mixture of potassium chlorate and manganese dioxide in ratio of 4:1. KClO<sub>3</sub> evolves oxygen at 375°C. At this temperature, it melts and converted into potassium perchlorate which decomposes at higher temperature to evolve oxygen. When MnO<sub>2</sub> is added, it starts giving oxygen at 250°C. Here MnO<sub>2</sub> acts as a catalyst.

 $MnO_2$  used for this purpose should be completely free from carbon as  $KClO_3$  and carbon mixture is explosive in nature. The mixture should be first heated gently and then strongly when it is ensured that there is no vigorous reaction.

#### Properties

Oxygen is a colourless, odourless and tasteless gas. It is little heavier than air and is slightly soluble in water. This small amount of dissolved oxygen in water supports the respiration of fish and other aquatic animals. It is soluble in alkaline pyrogallol. It can be liquefied to a pale blue liquid (b.pt.–183°C) by compressing the gas at a very low temperature. It is transformed into a blue solid on further cooling (freezing point = -218.4°C). Although  $O_2$  has an even number of electrons, two of them are unpaired, making the molecule **paramagnetic**; since it behaves like a tiny magnet and is attracted to a magnetic field. It exhibits allotropy. Its allotropic modification is ozone  $(O_3)$ . There are three isotopes of oxygen with mass numbers 16, 17 and 18 ( $O^{16}$ ,  $O^{17}$  and  $O^{18}$ ).  $O^{16}$  is the main one with an abundance of nearly 99.8%. The others are  $O^{17}$  (0.04%) and  $O^{18}$  (0.2%).

Oxygen is not a combustible gas, but it is a strong supporter of combustion. It is very active element. It directly combines with almost all metals (except noble metals) and non-metals (except zero group elements and halogens) and reacts with many compounds under suitable conditions. In fact, all the chemical reactions of oxygen are oxidation reactions. Except very few, the reactions with oxygen are exothermic in nature. A flame may also be produced in certain cases.

#### **■** Reactions with metals

(a) Active metals react at room temperature forming respective oxides.

$$4Na + O_2 \longrightarrow 2Na_2O$$
  
 $2Ca + O_2 \longrightarrow 2CaO$ 

However, Na, K, Rb, etc., further combine with oxygen to form peroxides and superoxides.

of in peroxides and superoxides.
$$M \xrightarrow{O_2} M_2O \xrightarrow{O_2} M_2O_2 \xrightarrow{O_2} MO_2$$
Normal oxide Peroxide Super oxide
$$(Li_2O) \qquad (Na_2O_2) \qquad (KO_2, RbO_2, CsO_2)$$

(b) Magnesium burns in atmosphere of  $O_2$  to form magnesium oxide.

$$2Mg + O_2 \longrightarrow 2MgO$$

(c) Metals like Fe, Al combine with dioxygen on heating.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$
  
 $4Fe + 3O_2 \longrightarrow 2Fe_2O_3$ 

#### **■** Reactions with nonmetals

Most of the nonmetals react with oxygen under high temperatures and form respective oxides. For example,

$$\begin{array}{c} \text{Hydrogen}: \ 2\text{H}_2 + \text{O}_2 & \xrightarrow{\text{or-electric} \\ \text{discharge}} & \text{Water} \\ \\ \text{Nitrogen}: \quad \text{N}_2 + \text{O}_2 & \xrightarrow{\text{3273 K}} & \text{2NO} \\ \text{Nitric oxide} \\ \\ \text{Sulphur}: \quad -\text{S} + \text{O}_2 & \xrightarrow{\text{Heat}} & \text{SO}_2 \\ \text{Sulphur dioxide} \\ \\ \text{Carbon}: \ 2\text{C} + \text{O}_2 & \xrightarrow{\text{Heat}} & \text{2CO} \\ \text{Carbon monoxide} \\ \\ \text{C} + \text{O}_2 & \xrightarrow{\text{Heat}} & \text{CO}_2 \\ \text{(Excess)} & \text{Carbondioxide} \\ \\ \text{Phosphorus}: \ \text{P}_4 + 5\text{O}_2 & \xrightarrow{\text{Heat}} & \text{P}_4\text{O}_{10} \\ \text{Phosphorus pentoxide} \\ \end{array}$$

#### **Reactions with compounds**

Oxygen is an oxidising agent. It oxidises many compounds under specific conditions. Some examples are given here.

$$2NO + O_2 \longrightarrow 2NO_2$$

$$4HCl + O_2 \xrightarrow{700 \text{ K}} 2H_2O + Cl_2 \quad \text{(Deacon's process)}$$

$$4NH_3 + 5O_2 \xrightarrow{1073 \text{ K}} 4NO + 6H_2O \quad \text{(Ostwald's process)}$$

$$2SO_2 + O_2 \xrightarrow{723 \text{ K}} 2SO_3 \quad \text{(Contact process)}$$

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow XCO_2 + \frac{y}{2}H_2O$$

#### Structure

The diatomic oxygen molecule has an unusual electronic structure. It is believed that two oxygen atoms in the molecule are bonded by a covalent double bond.

$$\ddot{\circ}$$
: $\ddot{\circ}$ : $\ddot{\circ}$ : $\ddot{\circ}$ : $\ddot{\circ}$ = $\ddot{\circ}$ :

However, the above structure is not supported by its paramagnetic nature. It has been suggested that between the two oxygen atoms only one covalent bond is established leaving two unpaired electrons, one in each atom.

This structure although can explain paramagnetic behaviour yet it does not explain high dissociation energy of oxygen molecule and does not conform to the octet rule.

Another structure, involving 3-electron bonds, has been suggested by **Pauling.** Two oxygen atoms are joined by one 2-electron bond and two 3-electron bonds. The structure accounts for two unpaired electrons and for the high dissociation energy but is contrary to octet rule.

$$:0$$
: $:0$ :

A better explanation for the existence of two unpaired electrons (paramagnetic behaviour) and a very high dissociation energy of  $O_2$  molecule has been provided by molecular orbital theory according to which the structure of  $O_2$  molecule is given below:

$$KK\sigma(2s)^2\sigma^*(2s)^2\sigma(2p_x)^2\pi(2p_y)^2\pi(2p_z)^2\pi^*(2p_y)^1\pi^*(2p_z)^1$$
  
Bond order in this case is  $\frac{1}{2}(8-4)=2$ 

#### **⊠** Uses

- (i) Oxygen mixed with helium or carbon dioxide is used for artificial respiration.
- (ii) Liquid oxygen is an important constituent of fuels used in rockets.
- (iii) Liquid oxygen mixed with finely divided carbon acts like a dynamite in coal mining.
- (iv) Oxygen is used for production of oxy-hydrogen or oxy-acetylene flames which are employed for cutting and welding purposes.
  - (v) Oxygen is used as an oxidising agent in several reactions.
- (vi) Oxygen is used in the manufacture of large number of compounds such as phenol, ethylene oxide, sulphur dioxide, sulphuric acid, nitric acid, chlorine, etc.
- (vii) <sup>18</sup>O is used as a tracer in the study of tracer mechanisms.

## 11.5 OXIDES

Oxygen combines nearly with all other elements except inert gases, noble metals and halogens. The binary compounds of oxygen with other elements are called oxides. However, the compounds of oxygen and fluorine (OF<sub>2</sub>, O<sub>2</sub>F<sub>2</sub>) are not called as oxides but oxygen fluorides as fluorine is more electronegative than oxygen.

Oxides may be prepared by the following general methods:

1. By burning of elements such as C, P, S, Na, K, Mg, etc., in air or oxygen atmosphere.

$$C + O_2 \longrightarrow CO_2$$
 (Carbon burns with flush light)  
 $S + O_2 \longrightarrow SO_2$  (Sulphur burns with blue light)  
 $4Na + O_2 \longrightarrow 2Na_2O$  (Sodium burns with yellow light)

$$4K + O_2 \longrightarrow 2K_2O$$
 (Potassium burns with violet light)  $2Mg + O_2 \longrightarrow 2MgO$  (Magnesium burns with white light)

2. By strongly heating carbonates, hydroxides or nitrates.

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

$$CuCO_3 \longrightarrow CuO + CO_2$$

$$2Ba(NO_3)_2 \longrightarrow 2BaO + 4NO_2 + O_2$$

(The carbonates, hydroxides of alkali metals do not decompose on heating and nitrates of alkali metals form nitrites on heating.)

3. The oxides of some of the non-metals and weak metals can be formed by the oxidation of the element with nitric acid.

C + 4HNO<sub>3</sub>(conc.) 
$$\longrightarrow$$
 CO<sub>2</sub> + 4NO<sub>2</sub> + 2H<sub>2</sub>O  
Si + 4HNO<sub>3</sub>(conc.)  $\longrightarrow$  SiO<sub>2</sub> + 4NO<sub>2</sub> + 2H<sub>2</sub>O  
Sn + 4HNO<sub>3</sub>(conc.)  $\longrightarrow$  SnO<sub>2</sub> + 4NO<sub>2</sub> + 2H<sub>2</sub>O

#### Classification of Oxides

(Based on Chemical Behaviour)

(i) Acidic oxides: The oxides which dissolve in water to form oxyacids are called acidic oxides. These are also called acid anhydrides of corresponding acids. The oxides combine with bases to form salts and water and with basic oxides form salts only.

These oxides are generally formed by non-metals. Examples are:

 $CO_2$ ,  $B_2O_3$ ,  $SiO_2$ ,  $N_2O_3$ ,  $NO_2$ ,  $N_2O_5$ ,  $P_4O_6$ ,  $P_4O_8$ ,  $P_4O_{10}$ ,  $SO_2$ ,  $Cl_2O_7$ ,  $I_2O_5$  and by metals in higher oxidation states such as  $SnO_2$ ,  $V_2O_5$ ,  $CrO_3$ ,  $Mn_2O_7$ , etc.

$$\begin{array}{c} \text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{CO}_3 \\ \text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 \\ \text{SO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_3 \\ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \longrightarrow \text{2HNO}_3 \\ \text{N}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow \text{2HNO}_2 \\ \text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \longrightarrow \text{4H}_3\text{PO}_3 \\ \text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \longrightarrow \text{4H}_3\text{PO}_4 \\ \text{Cl}_2\text{O}_7 + \text{H}_2\text{O} \longrightarrow \text{2HClO}_4 \\ \text{SnO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SnO}_3 \\ \text{Mn}_2\text{O}_7 + \text{H}_2\text{O} \longrightarrow \text{2HMnO}_4 \\ \text{CrO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{CrO}_4 \\ \end{array}$$

[Some of the oxides form two oxyacids. These are called mixed anhydrides.

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$
  
 $P_4O_8 + 6H_2O \longrightarrow 2H_3PO_3 + 2H_3PO_4$ 

$$\begin{array}{c} \text{SiO}_2 \ + \ 2\text{NaOH} \longrightarrow \text{Na}_2\text{SiO}_3 \ + \ \text{H}_2\text{O} \\ \text{Oxide} \qquad \text{Base} \qquad \qquad \text{Salt} \qquad \text{Water} \\ \\ B_2\text{O}_3 \ + \ 6\text{NaOH} \longrightarrow 2\text{Na}_3\text{BO}_3 \ + \ 3\text{H}_2\text{O} \\ \\ P_4\text{O}_{10} \quad + \ 12\text{NaOH} \longrightarrow 4\text{Na}_3\text{PO}_4 \ + \ 6\text{H}_2\text{O} \\ \text{Acidic oxide} \qquad \qquad \text{Salt} \\ \\ \text{SiO}_2 \ + \ \text{CaO} \longrightarrow \text{CaSiO}_3 \\ \\ \text{SO}_3 \ + \ \text{PbO} \longrightarrow \text{PbSO}_4 \\ \end{array}$$

(ii) Basic oxides: The oxides which either dissolve in water to form alkalies or combine with acids to form salts and water or combine with acidic oxides to form salts are called basic oxides. These oxides are formed by metals. Oxides may be ionic or covalent in nature.

$$Na_2O + H_2O \longrightarrow 2NaOH$$
 $CaO + H_2O \longrightarrow Ca(OH)_2$ 
 $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$ 
 $FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$ 
 $BaO + 2HC1 \longrightarrow BaCl_2 + H_2O$ 
 $PbO + SO_3 \longrightarrow PbSO_4$ 

(iii) Neutral oxides: The oxides which neither combine with acids nor with bases to form salts.

Examples: CO, H<sub>2</sub>O, N<sub>2</sub>O, NO, etc.

(iv) Amphoteric orides: The oxides which react with acids and bases both are termed amphoteric.

**Examples :** ZnO,  $Al_2O_3$ , BeO,  $Sb_2O_3$ ,  $Cr_2O_3$ , PbO,  $PbO_2$ , etc.

$$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$$
  
 $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$   
 $Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$   
 $Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$   
 $PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$   
 $PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O$   
 $Cr_2O_3 + 2NaOH \longrightarrow Na_2Cr_2O_4 + H_2O$   
 $Cr_2O_3 + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3H_2O$ 

(v) Compound or mixed oxides: Oxides which behave as mixture of two simple oxides.

#### **Examples:**

$$Pb_3O_4(2PbO + PbO_2)$$
,  $Fe_3O_4(FeO + Fe_2O_3)$ ,  $Mn_3O_4(2MnO + MnO_2)$ 

(vi) Peroxides: The oxides when treated with dilute acids form hydrogen peroxide. These oxides are considered as derivatives of  $H_2O_2$  and contain peroxo linkage in their molecules.

**Examples :** 
$$Na_2O_2$$
,  $K_2O_2$ ,  $BaO_2$ , etc.  
 $Na_2O_2 + H_2SO_4(dil.) \longrightarrow Na_2SO_4 + H_2O_2$ 

$$BaO_2 + H_2SO_4(dil.) \longrightarrow BaSO_4 + H_2O_2$$

Na<sub>2</sub>O<sub>2</sub> can be written as Na—O—O—Na. The linkage —O—O— is called peroxo linkage.

(vii) Dioxides: Like peroxides, these also contain excess of oxygen but do not form  $H_2O_2$  with dilute acids. They evolve chlorine with concentrated HCl and oxygen with concentrated  $H_2SO_4$ .

Examples: PbO<sub>2</sub>, MnO<sub>2</sub>

$$MnO_2 + 4HCl \text{ (conc.)} \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

$$2MnO_2 + 2H_2SO_4 \text{ (conc.)} \longrightarrow 2MnSO_4 + O_2 + 2H_2O$$

(viii) Suboxides: The oxides which contain less oxygen than expected from the normal valency of the elements are termed suboxides.

**Examples:** Carbon suboxide, C<sub>3</sub>O<sub>2</sub>; lead suboxide, Pb<sub>2</sub>O; nitrous oxide, N<sub>2</sub>O.

(ix) Superoxides: These oxides contain  $O_2^-$  ion. The superoxides known are  $KO_2$ ,  $RbO_2$  and  $CsO_2$ . These react with water to give hydrogen peroxide and oxygen.

$$12KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

#### 11.6 OZONE

**Historical:** In 1758, **Van Marum** observed a rotten smell when an electric discharge was passed through air. In 1840, **Schonbien** attributed that the rotten smell was due to formation of a new gas which he named **ozone**. The name ozone comes from the Greek word "ozo" meaning "smell". In 1866, **Sorret** established its formula, O<sub>3</sub>, and pointed out that the ozone is an allotrope of oxygen.

Occurrence: Ozone is present in sufficient amounts in the atmosphere at higher altitudes, *i.e.*, 12 to 15 miles above earth's surface. It is formed from oxygen present there, under the influence of ultraviolet rays from sun. Near earth's surface it is decomposed by dust particles. In small amounts, it occurs near the sea side or big lakes where it is formed by slow evaporation of water.

#### **Laboratory Preparation**

Ozone is obtained by passing silent electric discharge through dry oxygen. It is believed that some of the oxygen molecules dissociate and then atomic oxygen combines with oxygen molecules to form ozone.

$$O_{2} \xrightarrow{\text{Energy}} O + O$$

$$O_{2} + O \longrightarrow O_{3}$$

$$3O_{2} \Longrightarrow 2O_{3} - \text{energy}$$

The mixture obtained consists of 5-10% ozone by volume and the mixture is called **ozonised oxygen.** The apparatus used for this purpose is known as ozoniser. The commonly used ozonisers are:

(i) Siemen's ozoniser and (ii) Brodie's ozoniser

#### (i) Siemen's ozoniser

It consists of two concentric metal or glass tubes sealed together at one end (Fig. 11.7).

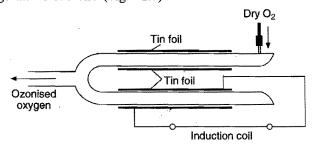


Fig. 11.7

The inner surface of inner tube and outer surface of the outer tube are coated with tin foil. The inner and outer coatings are connected with the two terminals of an induction coil. A current of dry oxygen at low temperature is passed in from one end. When the current is put on, the oxygen is partially converted into ozone. Ozonised oxygen come out from other end and is collected. It contains about 10% ozone, the percentage can be increased upto 15% if temperature is lowered to 5°C.

#### (ii) Brodie's ozoniser

It is shown in Fig. 11.8. The annular space is surrounded on both sides by dilute sulphuric acid in which platinum electrodes are dipped. These electrodes are connected to an

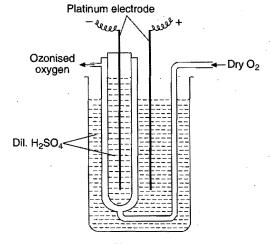


Fig. 11.8

induction coil. Oxygen passing through the annular space is subjected to silent electric discharge and is partially converted into ozone.

#### **Recovery of Pure Ozone from Ozonised Oxygen**

The ozonised oxygen is passed through a spiral cooled by liquid air. Ozone condenses as its condensation temperature is –112.4°C. The liquid ozone thus obtained may contain some dissolved oxygen. This liquid is fractionally distilled to get pure ozone.

#### **Some Reactions Forming Ozone**

(i) Fluorine reacts with water at a very low temperature when mixture of ozonised oxygen is formed.

$$\begin{array}{l}
2F_2 + 2H_2O \longrightarrow 4HF + O_2 \\
3F_2 + 3H_2O \longrightarrow 6HF + O_3
\end{array}$$
Ozonised oxygen

(ii) By action of ultra-violet rays, oxygen can be converted into ozone.

$$O_2 \xrightarrow{UV} O + O$$

$$O_2 + O \longrightarrow O_3$$

(iii) The electrolysis of acidified water with high current density and platinum anode yields ozone on the anode. Nascent oxygen discharged at anode combines with molecular oxygen to form ozone.

#### Properties

#### Physical properties:

- (a) It is a pale blue gas with a characteristic strong smell.
- (b) It can be liquefied to pale blue liquid at −112.4°C. At −249.7°C, it forms violet black crystals.
  - (c) It is heavier than air.
- (d) It is slightly soluble in water but more soluble in turpentine oil, glacial acetic acid, or carbon tetrachloride.
- (e) When inhaled in small amounts, it causes headache and nausea.
  - (f) It is diamagnetic in nature.

#### Chemical properties:

(a) **Decomposition:** It is unstable and decomposes completely into oxygen at 300°C.

$$2O_3 \xrightarrow{\text{Heat}} 3O_2 + 68 \text{ kcal}$$

 $MnO_2$ , platinum black, silver, lead dioxide, etc., decompose ozone at ordinary temperature, *i.e.*, they catalyse its decomposition.

**(b) Oxidising nature:** Due to the ease with which it can liberate nascent oxygen, it acts as a powerful oxidising agent. The potential equation is:

$$O_3 \longrightarrow O_2 + O$$

The oxidation potential in acid medium is +2.07 V.

$$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O \qquad E^\circ = +2.07 \text{ V}$$

[There are only three more substances which have oxidation potentials higher than +2.07 V. These are fluorine, atomic oxygen and oxygen fluoride, OF<sub>2</sub>]. Due to high value of oxidation potential it acts as a strong oxidising agent.

**Examples:** (i) It oxidises HCl into Cl<sub>2</sub>, HBr into Br<sub>2</sub> and HI into iodine.

$$O_{3} \longrightarrow O_{2} + O$$

$$2HCl + O \longrightarrow H_{2}O + Cl_{2}$$

$$2HCl + O_{3} \longrightarrow H_{2}O + Cl_{2} + O_{2}$$

(ii) Acidified ferrous sulphate into ferric sulphate.

$$\begin{array}{c}
O_3 \longrightarrow O_2 + O \\
\hline
2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O \\
\hline
2FeSO_4 + H_2SO_4 + O_3 \longrightarrow Fe_2(SO_4)_3 + H_2O + O_2
\end{array}$$

(iii) It liberates iodine from neutral KI solution.

$$O_{3} \longrightarrow O_{2} + O$$

$$2KI + H_{2}O + O \longrightarrow 2KOH + I_{2}$$

$$2KI + H_{2}O + O_{3} \longrightarrow 2KOH + I_{2} + O_{2}$$

(iv) Lead sulphide (black) is oxidised to lead sulphate (colourless).

$$\begin{array}{c}
[O_3 \longrightarrow O_2 + O] \times 4 \\
PbS + 4O \longrightarrow PbSO_4 \\
\hline
PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2
\end{array}$$

Similarly, CuS, ZnS and CdS are oxidised to  $CuSO_4$ ,  $ZnSO_4$  and  $CdSO_4$ , respectively.

(v) It oxidises nitrites into nitrates, sulphites into sulphates, arsenites to arsenates, manganate to permanganate and ferrocyanide to ferricyanide.

$$\begin{array}{c} NaNO_2 + O_3 \longrightarrow NaNO_3 + O_2 \\ Na_2SO_3 + O_3 \longrightarrow Na_2SO_4 + O_2 \\ Na_3AsO_3 + O_3 \longrightarrow Na_3AsO_4 + O_2 \\ Sodium \ arsenite \qquad Sodium \ arsenate \\ 2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2 \\ Potassium \\ manganate \qquad permanganate \\ 2K_4Fe(CN)_6 + H_2O + O_3 \longrightarrow 2K_3Fe(CN)_6 + 2KOH + O_2 \end{array}$$

$$2K_4Fe(CN)_6 + H_2O + O_3 \longrightarrow 2K_3Fe(CN)_6 + 2KOH + O_2$$
Potassium
ferrocyanide

Potassium
ferricyanide

(vi) Moist iodine is oxidised to iodic acid.

$$\frac{[O_3 \longrightarrow O_2 + O] \times 5}{I_2 + H_2O + 5O \longrightarrow 2HIO_3}$$

$$\frac{I_2 + H_2O + 5O_3 \longrightarrow 2HIO_3 + 5O_2}{Iodic acid}$$

Similarly; moist sulphur, phosphorus and arsenic are oxidised to their corresponding oxyacids.

$$\begin{array}{c} S + H_2O + 3O_3 \longrightarrow H_2SO_4 + 3O_2 \\ 2P + 3H_2O + 5O_3 \longrightarrow 2H_3PO_4 + 5O_2 \\ 2As + 3H_2O + 5O_3 \longrightarrow 2H_3AsO_4 + 5O_2 \end{array}$$

(vii) H<sub>2</sub>S is oxidised to sulphur.

$$H_2S + O_3 \longrightarrow H_2O + S + O_2$$

(viii) Alkaline KI is oxidised to potassium iodate and periodate.

$$KI + 3O_3 \longrightarrow KIO_3 + 3O_2$$
Potassium iodate

 $KI + 4O_3 \longrightarrow KIO_4 + 4O_2$ 
Pot. periodate

(ix) Dry iodine is oxidised to yellow powder, I<sub>4</sub>O<sub>9</sub>.

$$\begin{array}{c}
[O_3 \longrightarrow O_2 + O] \times 9 \\
2I_2 + 9O \longrightarrow I_4O_9 \\
\hline
2I_2 + 9O_3 \longrightarrow I_4O_9 + 9O_2
\end{array}$$

(x) Silver metal is blackened due to alternate oxidation of the metal and reduction of oxide.

$$\begin{array}{c} 2 Ag + O_3 \longrightarrow Ag_2O + O_2 \\ Ag_2O + O_3 \longrightarrow 2Ag + 2O_2 \end{array}$$

(xi) Mercury in presence of ozone is oxidised to suboxide which dissolves in mercury. It starts sticking to glass and loses mobility. Hence, mercury loses its meniscus in contact with ozone. This is termed as the tailing of mercury.

$$2Hg + O_3 \longrightarrow Hg_2O + O_2$$

(xii) Ozone reacts with KOH and forms potassium ozonide, KO3, which is an orange coloured solid and contains paramagnetic O<sup>3-</sup> ion.

$$2KOH + 5O_3 \longrightarrow 2KO_3 + 5O_2 + H_2O$$

In all above reactions, oxygen is evolved.

There are few reactions in which whole of the oxygen is used up in the process of oxidation.

1. Oxidises SO<sub>2</sub> to SO<sub>3</sub>.

$$3SO_2 + O_3 \longrightarrow 3SO_3$$

2. Acidified stannous chloride is oxidised to stannic chloride.

$$3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$$

(c) Bleaching property: It is a good bleaching agent. The bleaching action is due to its oxidising action on the organic matter.

It bleaches oil, ivory, flour, starch, waxes, wood pulp, etc.

(d) Formation of ozonides: Ozone reacts with unsaturated organic compounds containing double bonds. The products formed are known as ozonides. The ozonides break up when treated with water to form carbonyl compounds. The process is called **ozonolysis**. H<sub>2</sub>O<sub>2</sub> is evolved in most of the cases.

$$R$$
—CH = CH— $R'$  + O<sub>3</sub> — O CH $R'$ —O Ozonide

$$O \leftarrow CHR - O \rightarrow R - CH = O + R' - CH = O + H_2O_2$$

$$CHR' - O \rightarrow R - CH = O + R' - CH = O + H_2O_2$$
Mixture of Aldehydes

(e) Reaction with peroxide: Reaction of ozone with peroxide results in their mutual reduction with the liberation of oxygen.

$$BaO_2 + O_3 \longrightarrow BaO + 2O_2$$
  
 $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$ 

#### Uses

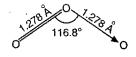
- (i) As a germicide and disinfectant for sterilizing water and improving the atmosphere of crowded places like tube railways, mines and cinema halls.
- (ii) As a bleaching agent for oils, flour, ivory, wax and delicate fabrics.
  - (iii) In the manufacture of artificial silk, synthetic silk,

synthetic camphor and potassium permanganate (by oxidation of potassium manganate).

- (iv) It is used for detecting the position of double bond in the unsaturated organic compounds.
- (v) In destroying odours that arise from cold storage rooms, kitchens of big hotels or slaughter houses.

#### Structure of Ozone

Trambaruls (1953) and Hughes (1956) have pointed out from the studies of ozone by electron diffraction that ozone molecule is V-shaped with a bond angle of 116.8° and O-O bond length 1.278 Å. The central oxygen atom in ozone is  $sp^2$ -hybridized.



The bond length is intermediate between that for a single bond (1.48 Å as in  $H_2O_2$ ) and for a double bond (1.21 Å as in O<sub>2</sub>). Ozone is, therefore, considered to be a resonance hybrid of the following two forms:

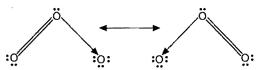


Fig. 11.10

**Tests of ozone:** (i) It has a strong rotten smell.

- (ii) Metallic mercury loses its fluidity in contact with ozone.
- (iii) It turns an alcoholic solution of benzidine brown.
- (iv) It turns an alcoholic solution of tetramethyl base violet.
- (v) It turns starch-iodide paper blue.

Ozone (O<sub>3</sub>)

#### Distinction between Ozone and Hydrogen Peroxide

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

1.	Pale blue gas with a strong rotten smell.	Colourless and odourless syrupy liquid.
2.	It does not decolourise acidified	It decolourises acidified potassium
	potassium permanganate.	permanganate.
3.	Mercury loses its meniscus in	No action on mercury.
	contact with ozone. It starts	Tro detion on mercury.
	sticking to glass.	
4.	It turns an alcoholic solution of	No action.
	benzidine brown.	110 delloil.
5.	It turns an alcoholic solution of	No action.
	tetramethyl base violet.	110 action.
6.	It does not turn starch-iodide	It turns starch-iodide paper blue in
	paper blue in presence of ferrous	presence of ferrous sulphate.
	sulphate.	presence of ferrous surpriate.
7.	No action with titanium	Orange colour with titanium
	sulphate solution.	sulphate solution is developed.
8.	No action with acidified	
٠.	potassium dichromate in	H <sub>2</sub> O <sub>2</sub> is added to mixture
	presence of ether.	containing potassium dichromate
	F	and concentrated H <sub>2</sub> SO <sub>4</sub> in
		presence of ether.
	,	prosoned of ener.



11.7 SULPHUR

The name sulphur has been derived from Sanskrit word *Sulveri* meaning killer of copper. The elementary nature of sulphur was established by **Lavoisier** in 1777.

**Occurrence:** It is widely distributed in nature both in free and combined state. The free sulphur is found in the volcanic regions of Sicily, Iceland, Japan, Mexico and Louisiana and Texas states of U.S.A. Sulphur in American deposits occurs at a depth of about 700–1200 feet while Sicily deposits are associated with 75% clay and gypsum. These are the two main sources of world supply of sulphur. In small quantities, it occurs in New Zealand, Russia, Baluchistan (Pakistan) and Kangra (India).

It occurs in abundance in the combined state as:

(i) **Sulphide ores,** e.g., Zinc blende or sphalerite (ZnS), galena (PbS), cinnabar (HgS), copper pyrites (CuFeS<sub>2</sub>) and iron pyrites (FeS<sub>2</sub>). Iron pyrite is called "fool's gold" because of its misleading resemblance to gold metal.

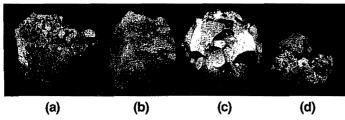


Fig. 11.11 Sulphide ores (from left to right): (a) Galena, PbS; (b) Cinnabar, HgS; (c) Pyrite, FeS<sub>2</sub>; and (d) Sphalerite, ZnS

- (ii) Sulphate ores, e.g., Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), barytes (BaSO<sub>4</sub>), Epsom salt (MgSO<sub>4</sub>·7H<sub>2</sub>O) and celesite (SrSO<sub>4</sub>).
- (iii) H<sub>2</sub>S and SO<sub>2</sub> in volcanic gases. H<sub>2</sub>S in spring waters, coal gas, sewage gas, etc.
- (iv) Organic compounds of plant and animal origin, e.g., onion, garlic, mustard, eggs, proteins, hair, wool, etc., contain organic sulphur compounds.

Sulphur is also found as deposits of the native element (brium-stone), which are formed by bacterial action on H<sub>2</sub>S.

**Extraction:** (i) To extract underground sulphur, **Frasch process** is used. Three concentric pipes are sunk deep into the ground. Super heated water at 170°C is forced down through the outer pipe into sulphur deposits, which heats the rock above the melting point of sulphur, 119°C. By this way sulphur gets melted. Compresed air blown through innermost pipe forcess the molten sulphur to come out through the third pipe,

as a liquid to the surface where it is allowed to solidify. 99.5% pure sulphur is obtained by this process.

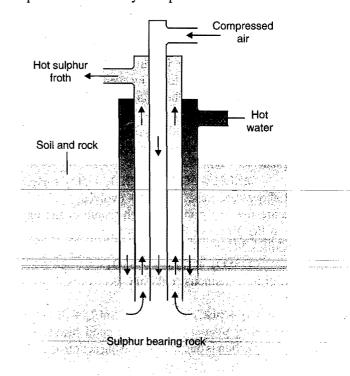


Fig. 11.12 The Frasch process for extraction of sulphur

(ii) Sulphur as a byproduct: (a) From alkali waste of Leblanc's process: The alkali waste (mainly CaS) is suspended in water and carbon dioxide is circulated. Hydrogen sulphide is liberated which is burnt in an insufficient supply of air.

$$CaS + H2O + CO2 \longrightarrow CaCO3 + H2S$$

$$2H2S + O2 \longrightarrow 2H2O + 2S$$
(Air)

(b) From the spent oxides of the gas works: It contains ferric sulphide  $(Fe_2S_3)$ . It is exposed to air for a few days when sulphur is deposited.

$$2Fe_2S_3 + 3O_2 \longrightarrow 2Fe_2O_3 + 6S$$

(c) From iron pyrites: Iron pyrites is a good source of sulphur. It is recovered when pyrite is distilled.

$$3FeS_2 \xrightarrow{\quad Distillation \quad } Fe_3S_4 + 2S$$

Pure sulphur is obtained by boiling impure sulphur at 444°C. The vapours of sulphur evolved are condensed on the cold walls as a light yellow powder.

#### Allotropic Forms

Sulphur exists in several allotropic forms, the important ones are described ahead:

1. Rhombic or octahedral or α-sulphur: This is the common form of sulphur. It is pale yellow in colour. It melts at 114.5°C. Its specific gravity is 2.06. It is insoluble in water but readily soluble in carbon disulphide. It dissolves to some extent in benzene, alcohol and ether. It is a crystalline variety and consists of S<sub>8</sub> structural units packed together into octahedral shape. This is the stable variety at ordinary temperature and all other forms gradually change into this form. This form gets converted into monoclinic form when heated above 96°C.

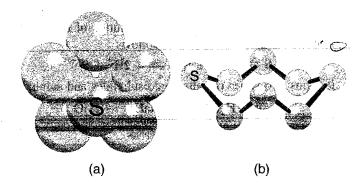


Fig. 11.13 Structure of S<sub>8</sub> molecule

2. Monoclinic or prismatic or  $\beta$ -sulphur: This form is formed by melting sulphur in a dish and cooling till crust is formed. Two holes are made in the crust and liquid is poured out. On removing the crust, needle shaped crystals of monoclinic sulphur are obtained.

This form of sulphur is stable above 95.6°C. The crystals are amber yellow in colour and have specific gravity of 1.96. Crystals melt at 119°C. It is also soluble in carbon disulphide. Below 95.6°C, it changes into rhombic form. Thus, 95.6°C is the transition temperature.

Rhombic sulphur 

95.6°C → Monoclinic sulphur

3. Plastic sulphur: This is obtained when boiling sulphur is poured into cold water. It is soft rubber like mass which hardens on standing and gradually changes into rhombic sulphur. It is amber-brown in colour and has specific gravity of 1.95. It is insoluble in CS<sub>2</sub> and has no sharp melting point. It consists of a completely random arrangement of chains of sulphur atoms.

#### Action of heat on sulphur

Ordinary sulphur melts at 114°C to a pale yellow mobile liquid. On heating further instead of becoming more mobile, it grows thicker. The colour changes to reddish brown and then to almost black. At about 180°C, the viscosity increases so much that it cannot be poured out by inverting the container. At about 200°C the viscosity begins to decrease and at its boiling point of 444°C, the liquid is again mobile. No definite explanation of these observations is known uptil now.

Uses: Sulphur is used:

- (i) in the manufacture of SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, CS<sub>2</sub>, matches, gun powder, fire works, etc.
- (ii) as a disinfectant for houses and for destroying bacteria, fungi, insects, etc. (vapours of sulphur are poisonous for bacteria, etc., but not for human beings).
- (iii) for vulcanising rubber and in the manufacture of sulphur dyes.
  - (iv) in medicine, for internal as well as external applications.

#### 11.8 COMPOUNDS OF SULPHUR

The main compounds of sulphur are,

- 1. Hydrogen sulphide or sulphuretted hydrogen (H<sub>2</sub>S)
- 2. Oxides of sulphur
- 3. Oxyacids of sulphur

#### 1. Hydrogen Sulphide or Sulphuretted Hydrogen (H<sub>2</sub>S)

**Occurrence:** It occurs in volcanic gases, sewage gases, coal gas and in several spring waters. It is found in small amounts in atmosphere, where it comes from the heating of coal and decay of animal and vegetable matter containing sulphur compounds.

**Laboratory preparation**: Hydrogen sulphide is obtained in the laboratory by the action of dilute sulphuric acid on ferrous sulphide.

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

As the gas is required intermittently in the laboratory, it is prepared in the well known Kipp's apparatus (Fig. 11.14).

The gas obtained is always impure as it is contaminated with hydrogen. Pure hydrogen sulphide can be prepared by the action of pure HCl on antimony sulphide.

$$Sb_2S_3 + 6HC1 \longrightarrow 2SbCl_3 + 3H_2S$$

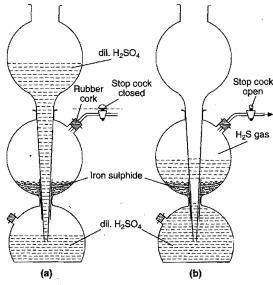


Fig. 11.14

#### **■** Properties

**Physical properties:** (a) It is a colourless gas with unpleasant odour of rotten eggs.

- (b) It is slightly heavier than air and moderatory soluble in cold water. The solubility decreases in hot water.
- (c) It is poisonous in nature. It produces headache when inhaled in small quantities but may cause death when inhaled for a long time.
- (d) It can be easily liquefied by pressure. The boiling point is about -60°C. It freezes to a transparent solid at -85.6°C.

**Chemical properties:** (a) Combustibility: The gas burns with a blue flame in oxygen or air forming sulphur dioxide and water.

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2$$

In restricted supply of oxygen, sulphur is formed due to incomplete combustion.

$$2H_2S + O_2 \longrightarrow 2H_2O + 2S$$

**(b) Thermal decomposition:** The gas is not so stable as water. It decomposes on heating. The decomposition starts at 310°C and completes at 1700°C.

$$H_2S \longrightarrow H_2 + S$$

- (c) Reducing nature: Hydrogen sulphide acts as a strong reducing agent as it decomposes evolving hydrogen. The following are the important examples of its reducing action:
  - (i) It reduces halogens into corresponding hydracids.

$$H_2S + X_2 \longrightarrow 2HX + S$$
  $(X_2 = F_2, Cl_2, Br_2 \text{ or } I_2)$ 

(ii) It reduces ferric chloride to ferrous chloride.

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$$

(iii) Sulphur dioxide is reduced to sulphur in presence of moisture.

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$

The occurrence of sulphur in volcanic regions is attributed due to the above reaction as both gases are present in volcanic gases.

(iv) H<sub>2</sub>O<sub>2</sub> is reduced to water.

$$H_2O_2 + H_2S \longrightarrow 2H_2O + S$$

(v)  $O_3$  is reduced to  $O_2$ .

$$H_2S + O_3 \longrightarrow H_2O + S + O_2$$

(vi) HNO<sub>3</sub> is reduced to NO<sub>2</sub>.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

$$H_2S + O \longrightarrow H_2O + S$$

$$2HNO_3 + H_2S \longrightarrow 2NO_2 + S + 2H_2O$$

(vii) H<sub>2</sub>SO<sub>4</sub> is reduced to SO<sub>2</sub>.

$$\begin{array}{c} H_2SO_4 \longrightarrow H_2O + SO_2 + O \\ H_2S + O \longrightarrow H_2O + S \\ \hline H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2 + S \end{array}$$

[Note:  $H_2S$  cannot be dried by conc.  $H_2SO_4$  because it oxidises  $H_2S$  to

It is therefore dried by passing through CaCl<sub>2</sub> or P<sub>4</sub>O<sub>10</sub>.]

(viii) Acidified KMnO<sub>4</sub> is decolourised.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$[H_2S + O \longrightarrow H_2O + S] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$

(ix) Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is reduced forming green chromic sulphate.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$
  
 $[H_2S + O \rightarrow H_2O + S] \times 3$ 

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

(d) Acidic nature: The aqueous solution of H<sub>2</sub>S acts as a weak dibasic acid. It ionises as follows:

$$H_2S \rightleftharpoons H^+ + HS^- \rightleftharpoons 2H^+ + S^-$$

It forms two series of salts, hydrosulphides and sulphides.

$$\begin{array}{c} NaOH + H_2S \longrightarrow \underset{Sodium\, hydro-}{NaHS} + H_2O \\ & \\ & \\ sulphide \end{array}$$

$$2NaOH + H_2S \longrightarrow Na_2S + 2H_2O$$
 Sodium sulphide

(e) Reaction with metals and metal oxides: H<sub>2</sub>S reacts with metals and metal oxides to form corresponding sulphides.

$$\begin{split} 2\text{Na} + \text{H}_2\text{S} &\longrightarrow \text{Na}_2\text{S} + \text{H}_2 \\ \text{Cu} + \text{H}_2\text{S} &\longrightarrow \text{CuS} + \text{H}_2 \\ 2\text{Ag} + \text{H}_2\text{S} &\longrightarrow \text{Ag}_2\text{S} + \text{H}_2 \\ \text{Pb} + \text{H}_2\text{S} &\longrightarrow \text{PbS} + \text{H}_2 \\ \text{CaO} + \text{H}_2\text{S} &\xrightarrow{\text{Heat}} \text{CaS} + \text{H}_2\text{O} \\ \text{ZnO} + \text{H}_2\text{S} &\xrightarrow{\text{Heat}} \text{ZnS} + \text{H}_2\text{O} \end{split}$$

- (f) Action on salts: Hydrogen sulphide reacts with salts of various metals forming corresponding sulphides. The metal sulphides can be divided into three groups.
- (i) Sulphides precipitated in acidic medium: These are sulphides of Hg, Ag, Pb, Cu, Bi, Cd, As, Sb and Sn.

$$\begin{array}{c} \text{CuSO}_4 + \text{H}_2\text{S} \longrightarrow \text{CuS} + \text{H}_2\text{SO}_4 \\ \text{Pb}(\text{CH}_3\text{COO})_2 + \text{H}_2\text{S} \longrightarrow \text{PbS} + 2\text{CH}_3\text{COOH} \\ \text{CdSO}_4 + \text{H}_2\text{S} \longrightarrow \text{CdS} + \text{H}_2\text{SO}_4 \\ \text{HgS}, \text{CuS}, \text{PbS} \longrightarrow \text{Black} \\ \text{Bi}_2\text{S}_3 \longrightarrow \text{Brown} \\ \text{CdS} \longrightarrow \text{Yellow} \end{array} \right\} \quad \begin{array}{c} \text{Insoluble in yellow} \\ \text{ammonium sulphide} \\ \text{SnS}_2, \text{As}_2\text{S}_3 \longrightarrow \text{Yellow} \\ \text{Sb}_2\text{S}_3 \longrightarrow \text{Orange} \\ \text{SnS} \longrightarrow \text{Chocolate} \end{array} \right\} \quad \begin{array}{c} \text{Soluble in yellow} \\ \text{ammonium sulphide} \\ \end{array}$$

(ii) Sulphides precipitated in alkaline medium: These are the sulphides of Zn, Co, Ni, Mn and Fe.

$$MnCl_2 + H_2S \longrightarrow MnS + 2HCl$$
  
 $Ni(NO_3)_2 + H_2S \longrightarrow NiS + 2HNO_3$ 

$$ZnSO_4 + H_2S \longrightarrow ZnS + H_2SO_4$$

CoS, NiS; Black, ZnS; White, MnS; Flesh coloured

- (iii) Sulphides which are precipitated neither in acidic nor in alkaline medium: These are the sulphides of Cr, Al, Mg, Ba, Sr, Ca, K and Na.
- (g) Formation of polysulphides: Polysulphides of metals are obtained by passing  $H_2S$  through their hydroxides.

$$Ca(OH)_2 + H_2S \longrightarrow CaS + 2H_2O$$
  
 $CaS + 4H_2S \longrightarrow CaS_5 + 4H_2$ 

On passing excess of H<sub>2</sub>S through ammonium sulphide, yellow ammonium sulphide is formed.

$$2NH_4OH + H_2S \longrightarrow (NH_4)_2S + 2H_2O$$

$$(NH_4)_2S + xH_2S \longrightarrow (NH_4)_2S_{x+1} + xH_2$$
Ammonium
polysulphide

#### Uses

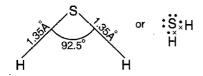
- (i) It is an important laboratory reagent for the detection of basic radicals in qualitative analysis.
- (ii) It is used for the preparation of metallic sulphides many of which find use in paint industry.
  - (iii) It is used as a reducing agent.

#### Tests of hydrogen sulphide

- (i) It has unpleasant odour resembling that of rotten eggs.
- (ii) It turns lead acetate paper black.
- (iii) It gives a violet colouration with a solution of sodium nitroprusside.

#### ■ Structure of H<sub>2</sub>S

The shape of the H<sub>2</sub>S molecule is similar to that of the water molecule, *i.e.*, V-shaped structure with bond length (H—S) 1.35 Å and bond angle (H—S—H) 92.5°.



#### 2. Oxides of Sulphur

Sulphur forms a number of oxides. These are:

- (i) Sulphur suboxide, S<sub>2</sub>O (colourless gas)
- (ii) Sulphur monoxide, SO (colourless gas)
- (iii) Sulphur sesquioxide, S<sub>2</sub>O<sub>3</sub> (green crystalline solid)
- (iv) Sulphur dioxide, SO<sub>2</sub> (colourless gas)
- (v) Sulphur trioxide, SO<sub>3</sub> (volatile liquid)
- (vi) Sulphur heptoxide, S<sub>2</sub>O<sub>7</sub> (liquid)
- (vii) Sulphur tetroxide, SO<sub>4</sub> (white solid)

Out of these, sulphur dioxide and sulphur trioxide are common and important and described here.

#### (i) Sulphur dioxide, SO<sub>2</sub>

**Preparation:** The following reactions can be used for the preparation of sulphur dioxide.

(a) By burning sulphur in air or oxygen.

$$S + O_2 \longrightarrow SO_2$$

Fig. 11.15 Structure of the SO<sub>2</sub> molecule

$$S + 2H_2SO_4 \xrightarrow{\text{Heat}} 2H_2O + 3SO_2$$

(c) By heating copper or silver with concentrated sulphuric acid.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$
  
 $2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + 2H_2O + SO_2$ 

(d) By reacting sodium sulphite or sodium hydrosulphite with dil. HCl.

$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$$
  
 $NaHSO_3 + HCl \longrightarrow NaCl + H_2O + SO_2$ 

(e) By roasting of sulphides.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$
  
 $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$ 

The reactions (b), (c) and (d) can be used for the preparation of  $SO_2$  in the laboratory while the reactions (a) and (e) are used in industry to obtain  $SO_2$ .

In places where gypsum or anhydrite are found in abundance, sulphur dioxide can be obtained on a large scale by heating gypsum or anhydrite with carbon at about 1000°C.

$$2CaSO_4 + C \longrightarrow 2CaO + 2SO_2 + CO_2$$

#### Properties

**Physical properties:** (a) It is a colourless gas with a pungent, suffocating odour.

- (b) It is heavier than air.
- (c) It is highly soluble in water.
- (d) It can be easily liquefied to a colourless liquid at  $-10^{\circ}$ C and into a snowlike solid at  $-76^{\circ}$ C.

**Chemical properties:** (a) It neither burns nor it helps in burning. However, burning magnesium and potassium continue to burn in its atmosphere.

$$3Mg + SO_2 \longrightarrow 2MgO + MgS$$

$$4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$$

**(b) Thermal decomposition :** It decomposes at 1200°C producing sulphur trioxide and sulphur.

$$3SO_2 \longrightarrow 2SO_3 + S$$

(c) Acidic nature: It is an acidic oxide. It dissolves in water forming sulphurous acid.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$
 (Sulphurous acid)

The gas is, therefore, known as sulphurous anhydride. It combines with basic oxides and forms sulphites.

$$BaO + SO_2 \longrightarrow BaSO_3$$

It reacts with alkalies forming two series of salts.

$$NaOH + SO_2 \longrightarrow NaHSO_3$$
  
Sod. bisulphite  
 $2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$   
Sod. sulphite

It also decomposes carbonates and bicarbonates evolving CO<sub>2</sub> gas.

$$Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2$$

Like CO<sub>2</sub>, it turns lime water milky due to the formation of CaSO<sub>3</sub>. However, if SO<sub>2</sub> is passed for a long time, milkiness disappears due to formation of soluble calcium bisulphite.

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O$$

$$(Milkiness)$$

$$CaSO_3 + H_2O + SO_2 \longrightarrow Ca(HSO_3)_2$$

$$Cal. \text{ bisulphite}$$

$$(soluble)$$

(d) Addition reactions: (i) It combines directly with halogens to form sulphuryl halides.

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$
 (Sulphuryl chloride)

(ii) It combines directly with oxygen in presence of a catalyst (platinised asbestos).

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

(iii) It directly combines with lead dioxide to form lead sulphate.

$$PbO_2 + SO_2 \longrightarrow PbSO_4$$

(e) **Reducing nature:** The aqueous solution of  $SO_2$  acts as a reducing agent as sulphurous acid changes into sulphuric acid giving nascent hydrogen.

$$H_2O + SO_2 \longrightarrow H_2SO_3$$
  
 $H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2H$ 

**Examples:** (i) It reduces halogens to their respective hydracids.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

$$2H + Cl_2 \longrightarrow 2HCl$$

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

(ii) Acidified KMnO<sub>4</sub> is reduced, i.e., it is decolourised.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$[SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H] \times 5$$
$$[2H + O \longrightarrow H_2O] \times 5$$

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

(iii) Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is turned green due to formation of chromic sulphate.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$[SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H] \times 3$$

$$[2H + O \longrightarrow H_2O] \times 3$$

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$
(Green)

(iv) Ferric sulphate is reduced to ferrous sulphate.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$
  
 $Fe_2(SO_4)_3 + 2H \longrightarrow 2FeSO_4 + H_2SO_4$ 

$$Fe_2(SO_4)_3 + SO_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

(v) It reduces acidified iodates to iodine.

$$[SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H] \times 5$$

$$2KIO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HIO_3$$

$$2HIO_3 + 10H \longrightarrow I_2 + 6H_2O$$

$$2KIO_3 + 5SO_2 + 4H_2O \longrightarrow K_2SO_4 + 4H_2SO_4 + I_2$$

- (f) Oxidising nature: It also acts as an oxidising agent particularly when treated with stronger reducing agents.
  - (i) It oxidises H<sub>2</sub>S into S.

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

(ii) Metals are oxidised by SO<sub>2</sub>.

$$3Mg + SO_2 \longrightarrow 2MgO + MgS$$
  
 $4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$   
 $3Fe + SO_2 \longrightarrow 2FeO + FeS$ 

(iii) CO is oxidised to CO<sub>2</sub> by SO<sub>2</sub>.

$$2CO + SO_2 \longrightarrow 2CO_2 + S$$

(iv) At 1000°C, it oxidises hydrogen into water.

$$SO_2 + 2H_2 \longrightarrow 2H_2O + S$$

(v) Stannous and mercurous salts are oxidised in presence of excess of HCl.

$$2\operatorname{SnCl}_2 + \operatorname{SO}_2 + 4\operatorname{HCl} \longrightarrow 2\operatorname{SnCl}_4 + 2\operatorname{H}_2\operatorname{O} + \operatorname{S}$$
  
 $2\operatorname{Hg}_2\operatorname{Cl}_2 + \operatorname{SO}_2 + 4\operatorname{HCl} \longrightarrow 4\operatorname{Hg}\operatorname{Cl}_2 + 2\operatorname{H}_2\operatorname{O} + \operatorname{S}$ 

(g) Bleaching action:  $SO_2$  in presence of moisture acts as a bleaching agent. This is due to the reducing nature of  $SO_2$ .

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

Coloured matter + H ---- Colourless matter

The bleaching is temporary. The bleached matter when exposed to air regains its colour due to oxidation.

#### Uses

- (i) It is used in the manufacture of sulphuric acid and paper from wood pulp (use of bisulphites).
- (ii) It is used as a bleaching agent for delicate articles like wool, silk and straw.
  - (iii) It is used in refining of petroleum and sugar.
- (iv) As a disinfectant for killing disease germs, fungi and certain moulds.

- (v) As a refrigerant in the form of liquid SO<sub>2</sub>.
- (vi) It is used as an antichlor for removing chlorine from a fabric after bleaching.

**Structure:** Already described in section 11.1 (3b).

#### (ii) Sulphur Trioxide, SO<sub>3</sub>

Preparation: Sulphur trioxide is obtained:

(i) by dehydrating sulphuric acid with excess of phosphorus pentoxide.  $6H_2SO_4 + P_4O_{10} \longrightarrow 4H_3PO_4 + 6SO_3$  Fig. 11.16 Structure



(ii) by heating ferric sulphate strongly. of the SO<sub>3</sub> molecule

$$Fe_2(SO_4)_3 \longrightarrow Fe_2O_3 + 3SO_3$$

(iii) by oxidation of SO<sub>2</sub> with oxygen in presence of a catalyst (commercial method).

$$2SO_2 + O_2 \stackrel{Pt}{\rightleftharpoons} 2SO_3$$

Both SO<sub>2</sub> and O<sub>2</sub> should be completely dry. The mixture is passed over platinised asbestos at 400°C, when SO<sub>3</sub> is formed.

#### **Properties**

- (i) SO<sub>3</sub> exists in three allotropic forms:
- (a)  $\alpha$ -SO<sub>3</sub>: It is chemically active form. If forms long transparent ice like crystals. The melting point of this form is 17°C.
- (b)  $\beta$ -SO<sub>3</sub>: It is dimeric (S<sub>2</sub>O<sub>6</sub>). It forms needle like silky white crystals. It melts at 32.5°C. Above 50°C, it changes to \alpha-form.
- (c)  $\gamma$ -SO<sub>3</sub>: It is like  $\beta$ -form and obtained by completely drying β-SO<sub>3</sub>. It melts at 62.2°C under 2 atmospheric pressure.
- (ii) SO<sub>3</sub> is an acidic oxide. It dissolves in water forming sulphuric acid with evolution of heat.

$$SO_3 + H_2O \longrightarrow H_2SO_4 + heat$$

It reacts with basic oxides forming sulphates.

$$CaO + SO_3 \longrightarrow CaSO_4$$
  
 $Na_2O + SO_3 \longrightarrow Na_2SO_4$ 

(iii) It dissolves in concentrated sulphuric acid forming oleum (fuming sulphuric acid).

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

(iv) It dissociates on heating at 1000°C into SO<sub>2</sub> and O<sub>2</sub>.

$$2SO_3 \xrightarrow{1000^{\circ}C} 2SO_2 + O_2$$

(v) It combines with concentrated hydrochloric acid and forms chloro-sulphonic acid, a derivative of sulphuric acid.

$$SO_3 + HCl \longrightarrow SO_2 \cdot (OH)Cl$$
Chloro-sulphonic acid

(vi) SO<sub>3</sub> acts as an oxidising agent.

Examples: 
$$2SO_3 + S \xrightarrow{100^{\circ}C} 3SO_2$$

$$5SO_3 + 2P \longrightarrow 5SO_2 + P_2O_5$$

$$SO_3 + PCl_5 \longrightarrow POCl_3 + SO_2 + Cl_2$$

$$\xrightarrow{Phosphoryl} \text{chloride}$$

$$SO_3 + 2HBr \longrightarrow H_2O + Br_2 + SO_2$$

#### Uses

- (i) In the manufacture of sulphuric acid and oleum.
- (ii) It is used as a drying agent for gases.

**Structure:** Already discussed in section 11.1 (3b).

#### 3. Oxyacids of Sulphur

A large number of oxyacids are known in the case of sulphur either in free state or in the form of salts or both. Oxyacids with S-S links are called thioacids. Acids having sulphur in lower oxidation state belong to -ous series while those having sulphur in higher oxidation state belong to -ic series. For

Sulphurous acid (H<sub>2</sub>SO<sub>3</sub>) O.N. sulphur, +4 Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) O.N. sulphur, +6

The following are main oxyacids of sulphur:

(1) Sulphurous acid series:	Oxidation Number
(i) Sulphurous acid, H <sub>2</sub> SO <sub>3</sub>	+4
(ii) Thiosulphurous acid, H <sub>2</sub> S <sub>2</sub> O <sub>2</sub>	+1
(iii) Hyposulphurous acid, H <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	+3
(iv) Pyrosulphurous acid, H <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	+4
(2) Sulphuric acid series:	
(i) Sulphuric acid, H <sub>2</sub> SO <sub>4</sub>	+6
(ii) Thiosulphuric acid, H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	
(iii) Pyrosulphuric acid, H <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	+6
(3) Thionic acid series:	
(i) Dithionic acid, H <sub>2</sub> S <sub>2</sub> O <sub>6</sub>	+5
(ii) Polythionic acid, $H_2S_nO_6$ ( $n = 3, 4, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5,$	, 6)

- (4) Peroxy acid series:
  - (i) Peroxy monosulphuric acid, H<sub>2</sub>SO<sub>5</sub> (Caro's acid)
  - (ii) Peroxy disulphuric acid, H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Marshall's acid) +6

Only two oxyacids (sulphurous acid and sulphuric acid) are described below:

#### (1) Sulphurous Acid, H<sub>2</sub>SO<sub>3</sub>

This acid is known only in solution. The solution is obtained by dissolving sulphur dioxide in water.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

The solution gives a smell of sulphur dioxide which is evolved completely on heating. It is, thus, believed that the acid is present in equilibrium with the free gas.

$$H_2SO_3 \rightleftharpoons H_2O + SO_2$$

Properties: It is a strong dibasic acid. It ionises in two stages.

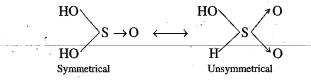
$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^-$$

It thus forms two series of salts. The salts are known as bisulphites (e.g., NaHSO<sub>3</sub>) and sulphites (e.g., Na<sub>2</sub>SO<sub>3</sub>). The salts are fairly stable.

Like SO<sub>2</sub>, it acts as a reducing agent and shows bleaching properties. These properties have been described under sulphur dioxide.

The acid also acts as an oxidising agent particularly when treated with strong reducing agents.

**Structure:** Sulphurous acid is believed to exist in two forms which are always in equilibrium with each other.



There is more evidence in favour of symmetrical formula,

(i) The preparation of sulphurous acid by the action of H<sub>2</sub>O on thionyl chloride supports symmetrical formula.

$$O \leftarrow S \qquad \begin{array}{c|c} \hline CI & H \\ \hline OH \\ \hline \hline CI & H \\ \hline OH \\ \end{array} \longrightarrow O \leftarrow S \qquad \begin{array}{c|c} OH \\ \hline OH \\ \hline OH \\ \end{array}$$

(ii) The molecule of sulphurous acid readily takes up oxygen or sulphur atom. This can be explained if symmetrical formula is accepted.

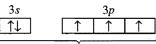
$$O \leftarrow S \xrightarrow{OH} O \xrightarrow{+O} S \xrightarrow{OH} OH$$

$$O \leftarrow S \xrightarrow{+S} OH OH$$

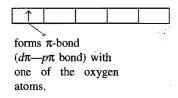
$$O \leftarrow S \xrightarrow{OH} OH$$

The unsymmetrical formula explains the reducing character due to presence of H-S bond and it also accounts for the formation of bisulphite HSO<sub>3</sub> ion.

X-ray analysis of the crystal of Na<sub>2</sub>SO<sub>3</sub> has revealed that SO<sub>3</sub><sup>2-</sup> ion has a pyramidal structure with three oxygen atoms in a triangle. This structure can be possible from sp<sup>3</sup> hybridization of excited sulphur atom giving a tetrahedral configuration



sp<sup>3</sup> hybridization (three sigma bonds with three oxygen atoms and one position occupied by lone pair)



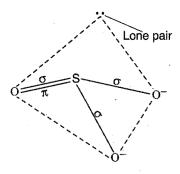


Fig.11.17 Pyramidal structure of SO<sub>3</sub><sup>2-</sup> ion

in which one position is occupied by a lone pair. This distorted tetrahedral structure reduces to pyramidal structure.

#### (2) Sulphuric Acid (oil of vitriol) H<sub>2</sub>SO<sub>4</sub>

Sulphuric acid is considered as the King of chemicals. The prosperity of any country is measured by the amount of sulphuric acid it consumes. Sulphuric acid is, thus, a substance of very great commercial importance as it is used practically in every important industry.

In ancient days, it was called oil of vitriol as it was prepared by distilling ferrous sulphate (Green vitriol).

$$\begin{array}{c} 2FeSO_4 \cdot 7H_2O \xrightarrow{\quad Heat \quad} Fe_2O_3 + H_2SO_4 + SO_2 + 13H_2O \\ \text{(Green vitriol)} \end{array}$$

Native sulphur is the starting material for the preparation of sulphuric acid. Sulphur is burnt and easily converted into sulphur dioxide. The conversion of sulphur dioxide into sulphur trioxide is a matter of difficulty. It requires either a catalyst or a strong oxidising agent. The trioxide dissolves in water to form sulphuric acid. The whole process may be summarised as:

$$S \longrightarrow SO_2 \longrightarrow SO_3 \longrightarrow H_2SO_4$$

For the oxidation of sulphur dioxide into sulphur trioxide. the following reactions may be used:

(i) By atmospheric oxygen in presence of a catalyst,  $V_2O_5$ , at 400°C,

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$5U_3 + H_2U \longrightarrow H_2SU_4$$

(ii) By Cl<sub>2</sub> or Br<sub>2</sub> in presence of moisture,

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$
  
 $SO_2 + 2H_2O + Br_2 \longrightarrow H_2SO_4 + 2HBr$ 

(iii) By H<sub>2</sub>O<sub>2</sub>,

$$SO_2 + H_2O_2 \longrightarrow H_2SO_4$$

(iv) By ozone (O<sub>3</sub>),

$$3SO_2 + O_3 \longrightarrow 3SO_3$$
,

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

(v) By conc. HNO<sub>3</sub>,

$$SO_2 + 2HNO_3 \longrightarrow H_2SO_4 + 2NO_2$$

#### Manufacture

Sulphuric acid is manufactured these days by the following two processes:

- (a) Lead chamber process
- (b) Contact process

#### ■ (a) Lead Chamber Process

**rinciple:** The mixture containing sulphur dioxide, air and nitric oxide when treated with steam, sulphuric acid is formed.

Nitric oxide acts as a catalyst in this reaction. Various mechanisms have been proposed for this reaction.

(i) Berzelius mechanism: Nitric oxide, NO combines with oxygen of the air and is oxidised to nitrogen dioxide (NO<sub>2</sub>).

$$2NO + O_2 \longrightarrow 2NO_2$$

SO<sub>2</sub> is oxidised by nitrogen dioxide into sulphur trioxide which reacts with steam forming sulphuric acid.

$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$
  
 $SO_3 + H_2O \longrightarrow H_2SO_4$ 

NO formed reacts again with oxygen of air and is oxidised to NO<sub>2</sub>. Thus, NO and NO<sub>2</sub> act as oxygen carriers.

(ii) Davy and Lunge mechanism: Nitroso-sulphuric acid is first formed as an intermediate product which then reacts with water forming sulphuric acid.

$$\begin{array}{c} NO + NO_2 \longrightarrow N_2O_3 \\ 2SO_2 + N_2O_3 + O_2 + H_2O \longrightarrow & 2HSO_4 \cdot NO \\ & & \text{Nitroso-sulphuric acid} \\ & & (Intermediate product) \\ 2HSO_4 \cdot NO + H_2O \longrightarrow 2H_2SO_4 + NO + NO_2 \end{array}$$

#### Working and Plant

The plant used for the manufacture of  $H_2SO_4$  in lead chamber process is shown diagrammatically in Fig. 11.18.

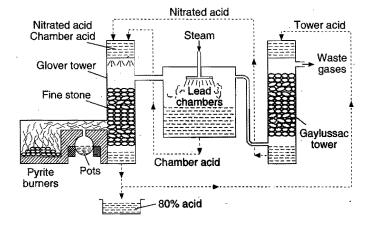


Fig. 11.18

The various parts of the plant and their functions are described below:

(a) **Pyrites or sulphur burners:** These are specially designed brick furnaces where iron pyrite or sulphur is burnt. The supply of air is regulated by sliding doors.

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$
$$S + O_2 \longrightarrow SO_2$$

- **(b) Dust chamber:** The dust chamber is provided with baffle walls where dust particles in the gaseous mixture coming from the burners separate due to gravity. This can also be done by using Cottrell electrostatic dust precipitator. [This part is not shown in Fig. 11.18:]
- (c) Nitre pots: Burner gases are then passed through a nitre oven in which potassium nitrate is heated with sulphuric acid. The nitric acid is decomposed by SO<sub>2</sub>.

$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$
  
 $2HNO_3 + 2SO_2 \longrightarrow 2SO_3 + H_2O + NO + NO_2$ 

In modern plants, oxides of nitrogen are produced by the catalytic oxidation of ammonia.

$$4NH_3 + 5O_2 \xrightarrow{\text{Pt. gauze}} 4NO + 6H_2O$$

$$2NO + O_2 \xrightarrow{} 2NO_2$$

- (d) Glover's tower: The tower is made of steel. It is lined inside with sheet of lead or acid resisting bricks. It is packed with flint stone or quartz. There are two tanks at the top. One tank contains the dilute chamber acid and other the nitrated acid from the base of the Gay-Lussac tower. Both these acids are mixed and then allowed to flow down slowly in Glover's tower. The gases are allowed to enter from the base of the tower. The following four functions occur in this tower:
  - (i) The gases are cooled down from about 400°C to 80°C.
  - (ii) Dilute chamber acid is concentrated.
  - (iii) The nitrated acid from Gay-Lussac tower is denitrated.  $2NO \cdot HSO_4 + H_2O \longrightarrow 2H_2SO_4 + NO + NO_2$
  - (iv) Some SO<sub>2</sub> is converted into H<sub>2</sub>SO<sub>4</sub>.

The sulphuric acid is collected at the bottom of the tower and is about 80%.

(e) Lead chambers: The gaseous mixture  $(SO_2$ , air, oxides of nitrogen) is then allowed to enter three or more large chambers made of lead and supported in wooden frames. Steam is admitted into these chambers from the top when dilute sulphuric acid is formed.

$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$
  
 $SO_3 + H_2O \longrightarrow H_2SO_4$ 

The acid is collected at the bottom of the chambers in a common receiver. This is known as chamber acid and contains 65–70% H<sub>2</sub>SO<sub>4</sub>. It is pumped to the top of Glover's tower for the concentration.

(f) Gay-Lussac tower: The residual gases mainly air and oxides of nitrogen from the lead chambers are allowed to

enter another tower called Gay-Lussac tower. This tower is lined with sheet lead packed with coke. A stream of cold concentrated sulphuric acid pumped from the base of Glover's tower flows down when it absorbs oxides of nitrogen from residual gases.

$$2H_2SO_4 + NO + NO_2 \longrightarrow 2NO \cdot HSO_4 + H_2O$$
Nitrated acid

This acid is pumped on the top of the Glover's tower.

The waste gases are allowed to escape through a chimney on the extreme right of the plant.

**Removal of impurities:** The chief impurities present in the sulphuric acid manufactured by lead chamber process are:

- (i) arsenious oxide (from pyrites).
- (ii) lead sulphate from the action of H<sub>2</sub>SO<sub>4</sub> on lead chamber.
- (iii) oxides of nitrogen.

These are removed as follows:

- (a) The acid is diluted with water when lead sulphate is precipitated which is filtered off.
- (b) Hydrogen sulphide is passed through dilute sulphuric acid which combines with arsenious oxide to form arsenious sulphide.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

Arsenious sulphide is filtered off.

(c) The acid is now distilled over ammonium sulphate when oxides of nitrogen are reduced to nitrogen.

$$(NH_4)_2SO_4 + NO + NO_2 \longrightarrow 2N_2 + 3H_2O + H_2SO_4$$

Usually, the chamber acid is not purified and is used as such for most of the purposes. Whenever pure  $H_2SO_4$  is needed, the acid manufactured by the contact process is used.

Concentration of chamber acid: The acid obtained from Glover's tower contains about 80%  $H_2SO_4$  and is known as brown oil of vitriol (B.O.V.) due to its colour. It can be further concentrated and the concentrated acid is called rectified oil of vitriol (R.O.V.). The concentration is done by evaporation of water present in the acid with the help of hot gases. Two methods are used for this purpose:

- (a) Cascade process and
- (b) Gaillard process.
- (a) Cascade process: A series of ferrosilicon dishes are arranged, one below the other, on a slope. The heating is done by means of hot gases playing below the dishes (Fig. 11.19). As the acid flows downwards, it is subjected to stronger heat, so that when it reaches the lowermost dish it has been concentrated to the maximum. Addition of ammonium sulphate during concentration helps to remove any dissolved oxides of nitrogen.

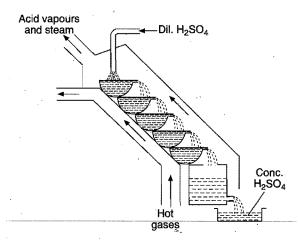


Fig. 11.19

(b) Gaillard process: The dilute acid is allowed to flow down in the form of a spray in a tower lined with acid resisting stone. Hot air enters from the base of the tower. The dilute acid comes in contact with hot air and loses water content. By the time the acid reaches the bottom, it becomes concentrated to about 95% (Fig. 11.20).

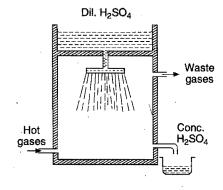


Fig. 11.20

#### **■** (b) Contact Process

**Principle:** This process involves the oxidation of sulphur dioxide by air in the presence of a catalyst.

$$2SO_2 + O_2 \stackrel{Catalyst}{\rightleftharpoons} 2SO_3$$

Sulphur trioxide is dissolved in 98% sulphuric acid when oleum is formed.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$
 (Oleum)

Sulphuric acid of any desired concentration can be obtained from oleum by dilution with water.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The oxidation of sulphur dioxide is reversible and exothermic.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 46.98 \text{ kcal}$$

According to Le-Chatelier principle, the favourable conditions for the greater yield of sulphur trioxide are:

- (a) An excess of air: Best results are obtained when  $SO_2$  and oxygen are present in molecular proportion of 2:3.
- (b) A low temperature: The optimum temperature is  $450^{\circ}$ C. Even at this temperature, the rate of reaction is slow and to accelerate the rate of reaction a catalyst is required. The commonly used catalysts are platinum, ferric oxide or vanadium pentoxide. Out of these, the best yield is obtained by the use of platinum. But it is very expensive and is easily poisoned by impurities. The purification of gases is done carefully when platinum is used as the catalyst. Nowadays, vanadium pentoxide  $(V_2O_5)$  is preferred as it is cheaper and not poisoned by impurities. However, it cannot be recovered after use.
- (c) A higher pressure: The optimum pressure for carrying the oxidation of sulphur dioxide is kept about one atmosphere.

#### Working and Plant

The manufacture of sulphuric acid involves three steps:

- (i) Production of sulphur dioxide
- (ii) Conversion of SO<sub>2</sub> into SO<sub>3</sub>
- (iii) Absorption of SO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub>

The plant used has been shown diagrammatically in Fig. 11.21.

The various parts of the plant and their functions are described below:

(a) Pyrite burners or sulphur burners: It is a kind of

furnace in which sulphur or iron pyrite is burnt to sulphur dioxide.

$$\begin{array}{c} S + O_2 \longrightarrow SO_2 \\ 4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2 \end{array}$$

The gases leaving the furnace contain SO<sub>2</sub>, air, dust particles and arsenious oxide.

(b) Purification unit: The gases are passed into dust chamber in which heavy dust particles are removed by mechanical precipitation aided by steam or electrically by using the Cottrell precipitator. The gases are now passed through cooling pipes and cooled to 100°C. The gases are led to steam scrubber where these are washed with steam or spray of water. The dust particles and impurities soluble in water are removed. If the catalyst is vanadium pentoxide, the gases should be made completely free from chlorine by using lime water in the scrubber.

The gases are dried by passing through the drying tower-packed with coke or flint stone. A steam of concentrated acid flows down in this tower. Finally, the gases are allowed to arsenic purifier which contains shelves holding ferric hydroxide. Ferric hydroxide absorbs arsenious oxide. The dry and pure mixture of SO<sub>2</sub> and air is then sent to the testing box in order to test the purity of the gas mixture.

(c) Preheater and contact tower: The dry and pure mixture of SO<sub>2</sub> and air is preheated to about 400°C are allowed to enter contact chamber (Fig. 11.22). It consists of iron cylinder containing a number of vertical pipes packed with platinised asbestos heated to about 450°C. SO<sub>2</sub> is oxidised to SO<sub>3</sub> by O<sub>2</sub> of the air. As this conversion is an exothermic reaction, the heat evolved maintains the temperature of the catalyst.

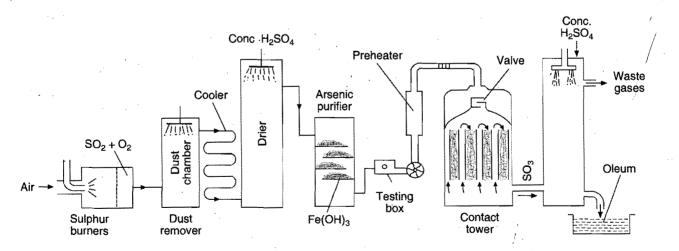


Fig. 11.21

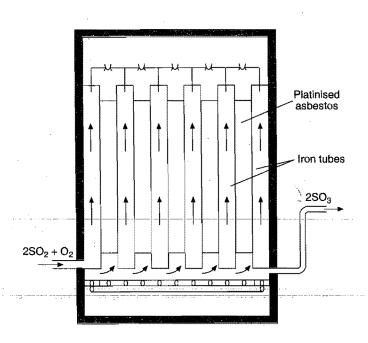


Fig. 11.22 Contact tower

(d) Absorption tower: The  $SO_3$  formed is passed up an absorption tower where it meets a descending stream of conc.  $H_2SO_4$ . The acid absorbs sulphur trioxide forming oleum (fuming sulphuric acid). The  $SO_3$  cannot be absorbed in water because it produces a dense fog which does not easily condense.

## COMPARISON BETWEEN THE LEAD CHAMBER AND CONTACT PROCESSES

	Lead chamber process	Contact process
1.	Catalyst used is a gas—nitric oxide.	Catalyst used is a solid vanadium pentoxide or platinum asbestos.
2.	Acid obtained is impure.	Acid obtained is pure.
3.	Acid obtained is 80%.	Oleum is obtained. Sulphuric acid of any concentration can be obtained from oleum.
4.	Methods of concentration of the acid are troublesome.	Further concentration is not necessary.
5.	It is not necessary to purify the gases.	It is absolutely necessary to purify the gases as impurities act as poison to catalyst.
6.	It is a cheaper method.	This method is costly. The cost has been reduced by the use of V <sub>2</sub> O <sub>5</sub> in place of platinum.

#### **Properties**

**Physical properties:** (a) It is a colourless syrupy liquid. It contains 98.3% sulphuric acid. Its specific gravity is 1.84 at 15°C. It has high viscosity because its molecules are associated due to hydrogen bonding.

- (b) It boils at 338°C (constant boiling mixture containing 98.3% H<sub>2</sub>SO<sub>4</sub> and 1.7% water). It freezes into colourless crystals at 10.5°C.
- (c) It fumes strongly in moist air and is highly corrosive in nature.
  - (d) It is a conductor of heat and electricity.
- (e) It is highly soluble in water. Various hydrates such as H<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>·3H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>·4H<sub>2</sub>O, are known. Heat is evolved when dissolved in water, usually bumping occurs. Due to this reason water should not be added to concentrated sulphuric acid for dilution but concentrated sulphuric acid should be added slowly to cold water with constant stirring. Due to its great affinity for water, it is used as a dehydrating substance.

#### Chemical properties:

(a) **Dissociation:** At 444°C, the vapours of sulphuric acid dissociate into steam and sulphur trioxide,

$$H_2SO_4 \Longrightarrow H_2O + SO_3$$

**(b) Acidic nature:** Dilute sulphuric acid is a strong dibasic acid. It ionises as:

$$H_2SO_4 \Longrightarrow H^+ + HSO_4^- \Longrightarrow 2H^+ + SO_4^{2-}$$

(i) It forms two series of salts with bases.

$$\begin{array}{c} \text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{H}_2\text{O}; \\ & \text{Sodium} \\ \text{bisulphate} \\ \\ 2\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \\ & \text{Sodium} \\ \text{sulphate} \\ \end{array}$$

(ii) It decomposes carbonates and bicarbonates into carbon dioxide.

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
  
 $NaHCO_3 + H_2SO_4 \longrightarrow NaHSO_4 + H_2O + CO_2$ 

(iii) It reacts with electropositive metals evolving hydrogen.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
  
Fe +  $H_2SO_4 \longrightarrow FeSO_4 + H_2$ 

(iv) It displaces more volatile acids from their metal salts.

$$\begin{split} 2NaCl &+ H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl \\ Ca_3(PO_4)_2 &+ 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4 \\ CaC_2O_4 &+ H_2SO_4 \longrightarrow CaSO_4 + H_2C_2O_4 \\ Calcium oxalate & Oxalic acid \end{split}$$

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

$$2CH_3COONa + H_2SO_4 \longrightarrow Na_2SO_4 + 2CH_3COOH$$

$$2NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_3$$

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

or.

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$$

$$\downarrow$$
 $NO + NO_2 + H_2O$ 

(c) Oxidising nature: It acts as a strong oxidising agent. The potential equation is:

$$\begin{array}{c} \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{O} + \text{SO}_2 + \text{O} \\ \text{(Hot conc.)} \\ \text{2H}_2\text{SO}_4 + 2e^- \longrightarrow \text{SO}_4^{2-} + 2\text{H}_2\text{O} + \text{SO}_2 \end{array}$$

(i) Non-metals such as carbon and sulphur are oxidised to their oxides.

$$[H_2SO_4 \longrightarrow H_2O + SO_2 + O] \times 2$$

$$C + 2O \longrightarrow CO_2$$

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$[H_2SO_4 \longrightarrow H_2O + SO_2 + O] \times 2$$

$$S + 2O \longrightarrow SO_2$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

Phosphorus is oxidised to orthophosphoric acid.

$$[H_2SO_4 \longrightarrow H_2O + SO_2 + O] \times 5$$

$$2P + 5O \longrightarrow P_2O_5$$

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

$$2P + 5H_2SO_4 \longrightarrow 2H_3PO_4 + 5SO_2$$

(ii) Metals like copper, silver, mercury, etc., are first oxidised by conc.  $H_2SO_4$  and then the oxides combine with acid to form corresponding sulphates.

$$\begin{array}{c} H_2SO_4 \longrightarrow H_2O + SO_2 + O \\ Cu + O \longrightarrow CuO \\ \hline CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \\ \hline Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O \\ \hline 2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + SO_2 + 2H_2O \\ Hg + 2H_2SO_4 \longrightarrow HgSO_4 + SO_2 + 2H_2O \\ \end{array}$$

(iii) Iodine is liberated from KI (HI is oxidised to I<sub>2</sub>)

$$2KI + H2SO4 \longrightarrow K2SO4 + 2HI$$

$$H2SO4 \longrightarrow H2O + SO2 + O$$

$$2HI + O \longrightarrow H2O + I2$$

$$2KI + 2H2SO4 \longrightarrow K2SO4 + SO2 + I2 + 2H2O$$

Similarly, bromine is liberated from KBr (HBr is oxidised to Br<sub>2</sub>).

$$2KBr + 2H_2SO_4 \longrightarrow K_2SO_4 + SO_2 + Br_2 + 2H_2O$$

(iv) In presence of Hg as a catalyst, naphthalene is oxidised to phthalic acid.

$$C_{10}H_8 + 9H_2SO_4 \longrightarrow C_8H_6O_4 + 10H_2O + 9SO_2 + 2CO_2$$
Phthalic acid

(d) Dehydrating nature: As sulphuric acid has great affinity for water, it acts as a powerful dehydrating agent. Its

corrosive action on skin is also due to dehydration of skin. It absorbs water from organic compounds.

$$\begin{array}{c} C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C \\ C_{ane \ sugar} \xrightarrow{(-11H_2O)} 12C \\ C_6H_{12}O_6 \xrightarrow{H_2SO_4} 6C \\ Glucose \xrightarrow{(-6H_2O)} 6C \\ (COOH)_2 \xrightarrow{(-H_2O)} CO + CO_2 \\ Oxalic \ acid \xrightarrow{(-H_2O)} CO \\ Formic \ acid \xrightarrow{(-H_2O)} CO \\ Ethyl \ alcohol \xrightarrow{(-H_2O)} C_2H_5OC_2H_5 \\ \hline Ethyl \ alcohol \ Ether \\ \end{array}$$

Cloth, wood, starch, paper, etc., are all charred in concentrated sulphuric acid.

#### (e) Miscellaneous reactions:

(i) **Sulphonation**: Aromatic compounds react with sulphuric acid forming sulphonic acids.

$$\begin{array}{c} C_6H_6 + H_2SO_4 & \longrightarrow C_6H_5SO_3H + H_2O \\ \text{Benzene} & \text{Benzene} \\ \text{sulphonic acid} \end{array}$$

(ii) Action of PCl<sub>5</sub>: The molecule of sulphuric acid contains two hydroxyl groups. One or both the hydroxyl groups can be replaced by chlorine when treated with PCl<sub>5</sub>.

OH 
$$O_2S$$
  $OH + PCl_5 \longrightarrow O_2S$   $OH + PCl_3 + HCl$   $OH + PCl_5 \longrightarrow O_2S$   $OH + PCl_5 \longrightarrow OH$   $O$ 

(iii) On heating potassium ferrocyanide with concentrated sulphuric acid, carbon monoxide is evolved.

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \longrightarrow$$
  
 $2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$ 

(iv) On heating potassium chlorate with concentrated sulphuric acid, chlorine dioxide is evolved with explosion.

$$3KClO_3 + 3H_2SO_4 \longrightarrow 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$$

(v) Sulphuric acid reacts with barium and lead salts to form insoluble sulphates. These sulphates are even insoluble in conc. HCl and conc. HNO<sub>3</sub>.

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$$
  
 $Pb(NO_3)_2 + H_2SO_4 \longrightarrow PbSO_4 + 2HNO_3$ 

(vi)  $H_2SO_4$  absorbs sulphur trioxide forming oleum or fuming sulphuric acid.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$
Oleum

(vii) H<sub>2</sub>SO<sub>4</sub> when treated with phosphorus pentoxide loses water and forms sulphur trioxide.

$$H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$$

### Uses

It is used:

- (i) for the manufacture of fertilizers such as ammonium sulphate and superphosphate of lime.
- (ii) in the manufacture of other acids such as hydrochloric acid, orthophosphoric acid, nitric acid, etc.
- (iii) in the manufacture of explosives such as, nitroglycerine, gun cotton, TNT (trinitro-toluene), picric acid, etc.
- (iv) in the manufacture of important chemicals such as sodium carbonate, alums, metal sulphates, ethers, phosphorus, etc.
  - (v) in the refining of petroleum.
- (vi) in the manufacture of coal-tar dyes and a number of drugs and disinfectants.
  - (vii) in the textile, paper and dyeing industries.
  - (viii) in the leather industry for tanning.
- (ix) for cleansing metals before electroplating, enameling, galvanising, etc., (Pickling).
  - (x) in storage batteries.
  - (xi) in manufacturing paints and pigments.
- (xii) as an important laboratory reagent. In organic chemistry it is used for synthesis of various organic compounds and sulphonation reactions. It is also used as an oxidising and a dehydrating agent.

**Structure:** Sulphuric acid has two OH groups which are directly attached to sulphur. The molecule has been assigned the following structure:

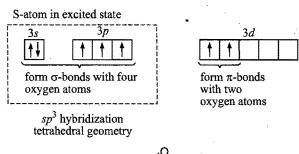
The sulphate ion,  $SO_4^{2-}$ , is therefore, represented as

$$\begin{bmatrix} O \\ \uparrow \\ O - S - O \\ \downarrow \\ O \end{bmatrix}^{2-}$$

However, the ion shows a considerable amount of double character as the bond lengths are all rather short. Thus, the sulphate ion is a resonance hybrid, as represented below:

The unionised acid is, therefore, resonance hybrid of the following two structures:

In crystals,  $SO_4^{2-}$  ion has a tetrahedral structure. This can be explained on the basis of  $sp^3$  hybridization.



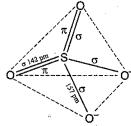


Fig.11.23 Tetrahedral geometry of SO<sub>4</sub><sup>2-</sup> ion

### Tests for H<sub>2</sub>SO<sub>4</sub>:

- (1) When heated with copper, it evolves  $SO_2$  which has a characteristic smell. The gas reacts with acidified  $K_2Cr_2O_7$  solution which is turned green.
- (2) It forms white precipitate with barium chloride solution which is insoluble in conc. HCl and conc. HNO<sub>3</sub>.
- (3) When heated with NaCl, it evolves HCl which forms white fumes with NH<sub>4</sub>OH.

## SOME SOLVED PROBLEMS

**Example 1.** A is a binary compound of univalent metal. 1.422 g of A reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid, B, that forms a hydrated double salt, C, with  $Al_2(SO_4)_3$ . Identify A, B and C. [1.1.T.1994]

### **Solution:**

As the solid B forms a hydrated double salt with  $Al_2(SO_4)_3$ , it should be a sulphate of a univalent metal,  $M_2SO_4$ .

One molecule of sulphate contains one sulphur atom, *i.e.*, the mass of the sulphate which contains 32.1 g sulphur should be its molecular mass.

0.321 g sulphur is present in (1.422 + 0.321 = 1.743 g) of B.

32.1 g of sulphur is present in 
$$=\frac{1.743}{0.321} \times 32.1 = 174.3$$
 g

Let the atomic mass of univalent metal be x.

$$M_2SO_4 = 2x + 32.1 + 64.0 = 174.3$$
or
$$2x = 78.2$$

$$x = 39.1$$

Atomic mass 39.1 corresponds to potassium.

Thus, the compound B is  $K_2SO_4$  and the compound C is  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ .

Since, B is formed with interaction of A and sulphur, A must be an oxide of potassium (most probably  $KO_2$ ).

$$2KO_2 + S_{2 \times 71.1} \xrightarrow{32.1} K_2SO_4$$

32.1 g of S reacts with  $A = 2 \times 71.1$  g

0.321 g of S reacts with 
$$A = \frac{2 \times 71.1}{32.1} \times 0.321 = 1.422$$
 g

Thus, A is supported by the given data.

A is, therefore, potassium superoxide,  $KO_2$ .

**Example 2.** When gas A is passed through dry KOH at low temperature, a deep red coloured compound, B and a gas C are obtained. The gas A, on reaction with but-2-ene, followed by treatment with  $Zn/H_2O$  yields acetaldehyde. Identify A, B and C. [LI.T. 1994]

### Solution:

The reaction of gas A with but-2-ene followed by treatment with  $Zn/H_2O$  suggests that A is  $O_3$ .

Reaction with KOH
$$2\text{KOH} + 5\text{O}_3 \longrightarrow 2\text{KO}_3 + 5\text{O}_2 + \text{H}_2\text{O}$$

$$(A) \qquad (B) \qquad (C)$$
(Deep red coloured)

**Example 3.** How you will obtain the following from sulphuric acid?

(i)  $SO_2$  (ii)  $SO_3$  (iii)  $SO_2Cl_2$  (iv)  $H_2S$  (v) S.

### Solution:

(i)  $SO_2$  is obtained by heating copper with conc.  $H_2SO_4$ — $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$ It can also be obtained by boiling sulphur with conc.  $H_2SO_4$ .

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

(ii) H<sub>2</sub>SO<sub>4</sub> when treated with P<sub>2</sub>O<sub>5</sub> loses water and forms SO<sub>3</sub>.

$$H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$$

(iii) SO<sub>2</sub>Cl<sub>2</sub> is formed when conc. H<sub>2</sub>SO<sub>4</sub> is treated with excess of PCl<sub>5</sub>.

$$H_2SO_4 + 2PCl_5 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$

(iv) and (v) H<sub>2</sub>S and S are obtained from conc. H<sub>2</sub>SO<sub>4</sub> by the following reactions.

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 \xrightarrow{4C} BaS \xrightarrow{HCl} H_2S \xrightarrow{Oxid.} S$$

### Example 4. Explain the following:

- (i) An acidified  $K_2Cr_2O_7$  paper turns green when exposed to  $SO_2$ .
- (ii)  $H_2S$  acts only as reducing agent while  $SO_2$  can act both as a reducing agent and an oxidising agent.
  - (iii) SO2 acts as a bleaching agent.
  - (iv) Sugar turns black on addition of conc. H<sub>2</sub>SO<sub>4</sub>.
  - (v) Ozone destroys mercury meniscus.
  - (vi) SF<sub>6</sub> is known but SH<sub>6</sub> is not known.

### **Solution:**

(i) Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> acts as an oxidising agent in presence of SO<sub>2</sub> and converted into chromium compound which is green in colour.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O_3SO_2 + 3O_4 + 3H_2O \longrightarrow 3H_2SO_4$$

$$\overline{\text{K}_2\text{Cr}_2\text{O}_7}$$
 +  $\overline{\text{H}_2\text{SO}_4}$  +  $\overline{\text{3SO}_2}$   $\longrightarrow$   $\overline{\text{K}_2\text{SO}_4}$  +  $\overline{\text{Cr}_2(\text{SO}_4)_3}$  +  $\overline{\text{H}_2\text{O}}$ 

(ii) On the basis of electronic configuration  $(3s^23p^4)$ , the maximum and minimum oxidation states of S are +6 and -2.

In  $H_2S$ , the oxidation state of S is -2. It can increase only oxidation state and cannot decrease. Thus,  $H_2S$  can act only as a reducing agent. In  $SO_2$ , the oxidation state is +4, *i.e.*, it can be increased as well as decreased. Thus,  $SO_2$  can act both as a reducing agent and an oxidising agent.

(iii)  $SO_2$  in presence of moisture is oxidised to  $H_2SO_4$  liberating nascent hydrogen. The nascent hydrogen bleaches the coloured substance.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$

Coloured substance  $+ 2[H] \longrightarrow Colourless$ 

(iv) Conc. H<sub>2</sub>SO<sub>4</sub> has great affinity for water molecules, *i.e.*, it acts as a dehydrating agent. When in contact with sugar, all water molecules are taken up and carbon is left behind.

$$C_{12}H_{22}O_{11} \xrightarrow{Conc. H_2SO_4} 12C + 11H_2O$$

(v) Ozone acts as a strong oxidising agent. It oxidises mercury into mercurous oxide which starts sticking to glass. Mercury loses its mobility, *i.e.*, mercury meniscus is destroyed.

$$2Hg + O_3 \longrightarrow Hg_2O + O_2$$

(vi) In the highest oxidation state, sulphur can combine only with highly electronegative element like fluorine and not hydrogen. Hence, sulphur forms SF<sub>6</sub> but not SH<sub>6</sub>.

**Example 5.** State with balanced equation what happens when?

- (a) Potassium ferrocyanide is heated with conc.  $H_2SO_4$ .
- (b) A mixture of potassium chlorate, oxalic acid and sulphuric acid is heated.
  - (c) Sodium chlorate reacts with sulphur dioxide.
- (d) Chlorine gas is passed into water saturated with hydrogen sulphide. [M.L.N.R. 1991]
- (e) Hydrogen sulphide is passed through sodium bisulphite solution. [I.J.T. 1991]

### **Solution:**

(a) CO is evolved.

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \longrightarrow$$
  
 $2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$ 

(b) Potassium chlorate is reduced while oxalic acid is oxidised.

$$KClO_3 + H_2SO_4 \longrightarrow KHSO_4 + HCl + 3O$$
  
 $3H_2C_2O_4 + 3O \longrightarrow 6CO_2 + 3H_2O$ 

$$KClO_3 + 3H_2C_2O_4 + H_2SO_4 \longrightarrow KHSO_4 + HCl + 6CO_2 + 3H_2O_4$$

(c) NaClO<sub>3</sub> is reduced to NaCl.

$$[SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H] \times 3$$
  
NaClO<sub>3</sub> + 6H  $\longrightarrow$  NaCl + 3H<sub>2</sub>O

$$NaClO_3 + 3SO_2 + 3H_2O \longrightarrow 3H_2SO_4 + NaCl$$

(d) 
$$Cl_2 + H_2S \longrightarrow 2HCl + S$$

(e) 
$$2NaHSO_3 \longrightarrow Na_2SO_3 + H_2O + SO_2$$
$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$$
$$2NaHSO_3 + 2H_2S \longrightarrow Na_2SO_3 + 3S + 3H_2O$$

**Example 6.** Sulphur melts to form a clear mobile liquid at 119°C but on further heating to 180°C, it becomes viscous. Why?

### Solution:

Upto 119°C, sulphur exists as S<sub>8</sub> molecules which can roll over one another to form a mobile liquid. However, when this liquid is further heated to 180°C, the cleavage of ring structure occurs and zig-zag open chains are formed which get interwound and tangled together and hence sulphur becomes more viscous.

**Example 7.** SOCl<sub>2</sub> can act as a weak Lewis acid as well as a weak Lewis base. Explain.

### Solution:

Like nitrogen in ammonia, sulphur has a lone pair of electrons which it can donate, hence it acts as a weak base.

 $SOCl_2$  has also empty *d*-orbitals which can accommodate electron pairs from bases and hence acts as a weak acid.

**Example 8.** (a) Which form of sulphur does show paramagnetic nature? Explain.

- (b) Compounds of fluorine and oxygen are called fluorides and not oxides. Explain.
- (c) Sulphur disappears when boiled with an aqueous solution of sodium sulphite. Why?

### **Solution:**

- (a) In vapour state, sulphur partly exists as  $S_2$  molecules and  $S_2$  molecule like  $O_2$  molecule has two unpaired electrons in the antibonding  $\pi$ -orbitals and exhibits paramagnetic nature.
- (b) This is because of higher electronegativity of fluorine than oxygen. In naming a compound, the electropositive or less electronegative element is taken first, thus, the compounds of fluorine and oxygen are called oxygen fluorides and fluorine oxides.
- (c) Sulphur combines with sodium sulphite and forms sodium thiosulphate which is soluble in water and hence S disappears.

**Example 9.** Knowing the electron gain enthalpy values for  $O \longrightarrow O^-$  and  $O \longrightarrow O^{2-}$  as  $-141 \text{ kJ mol}^{-1}$  and  $702 \text{ kJ mol}^{-1}$  respectively, how can you account for the formation of a large number of oxides having  $O^{2-}$  species and not  $O^-$ ?

### Solution:

Although the formation of  $O^{2-}$  anion requires more energy in comparison to the formation of  $O^{-}$  anion factually energy is released), yet in large number of oxides, oxygen is divalent in nature. This is due to the fact that lattice energies of the oxides having  $O^{2-}$  anions are very high on account of greater magnitude of electrostatic forces of attraction.

**Example 10.** Give at least one example to explain the following properties:

- (i) Sulphuric acid is a dibasic acid.
- (ii) Sulphuric acid is a dehydrating agent.
- (iii) Sulphuric acid is an oxidising agent.

### Solution:

(i) H<sub>2</sub>SO<sub>4</sub> forms two series of salts, *i.e.*, both the hydrogen atoms are replaceable.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^- \longrightarrow 2H^+ + SO_4^{2-}$$
 $H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$ 
Sodium hydrogen
Sulphate (acid salt)

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$
Sodium sulphate
(Normal salt)

(ii) H<sub>2</sub>SO<sub>4</sub> has great affinity for water molecules and hence, acts as a dehydrating agent.

$$\text{HCOOH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{H}_2\text{O} + \text{CO}$$

(iii) H<sub>2</sub>SO<sub>4</sub> oxidises metals, nonmetals and other compounds.

Cu + 
$$2H_2SO_4(conc.) \longrightarrow CuSO_4 + SO_2 + 2H_2O$$
  
 $S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$   
 $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$ 

# SUMMARY AND IMPORTANT POINTS TO REMEMBER

- 1. Group 16 or VIA of the periodic table consists of six elements—oxygen, sulphur, selenium, tellurium, polonium and ununhexium. These elements are called **chalcogens**, *i.e.*, ore forming elements. These are *p*-block elements as the last differentiating electron is accommodated on *np* shell. All have six electrons in their outermost shell, *i.e.*, *ns*<sup>2</sup>*np*<sup>4</sup> configuration.
- 2. The elements oxygen and sulphur are common while selenium, tellurium and polonium are comparatively rare. Oxygen is the most abundant element. It makes up 46.6% by mass of the earth's crust. It is found both in free and combined state. Sulphur is the sixteenth most abundant element. It occurs mainly in the combined form. The last member is radioactive in nature.
- 3. Oxygen is a gas while other members of group 16 are solids. Oxygen is a diatomic molecule while the molecules of other members are complex. Sulphur, selenium and tellurium exist as 8-atom staggered rings. In S<sub>8</sub> molecule, each S-atom is sp<sup>3</sup> hybridized involving both bonding and non-bonding electron pairs.

Oxygen atom is capable to form multiple bonds ( $p\pi$ - $p\pi$  interaction) with other oxygen atom on account of small size. However, this tendency is missing in sulphur atom. The bond energy of oxygen-oxygen double bond is quite high as compared to oxygen-oxygen single bond. In sulphur, the sulphur-sulphur double bond energy is not so large in comparison to single bond energy. As a result -O-O-O—chains are less stable as compared to O=O molecule while -S-S-S—chains are more stable than S=S molecule. Thus, oxygen exists as a diatomic gas molecule, sulphur exists as  $S_8$  solid.

The diatomic molecule O=O accounts for high dissociation energy but does not explain paramagnetic nature. Pauling proposed 3-electron bond structure :O:•••O: to explain paramagnetic behaviour.

4. (a) Metallic character increases with increase in atomic number.

- (b) Atomic radii, atomic volume and density increase gradually from O to Po.
- (c) Electronegativity decreases gradually. Oxygen is second most electronegative element.
- (d) The melting and boiling points increase gradually from O to Po.
- (e) The ionisation potential values are high and decrease gradually. The elements do not lose the electrons to form positive ions easily.
- (f) All the members show allotropy. Oxygen: Ordinary oxygen and ozone are allotropic forms. Sulphur: Rhombic, monoclinic, plastic and amorphous are allotropic forms.
- Selenium: Red form and grey form are allotropic forms.

  (g) Oxygen and sulphur show the property of catenation but this property is more pronounced in sulphur.
- 5. All these elements have six electrons in their valency shell. They complete the octet either (a) by forming bivalent anion gaining two electrons such as:

 $O^{2-}$ ,  $S^{2-}$ ,  $Se^{2-}$  and  $Te^{2-}$  showing electrovalency (di). or (b) by forming two covalent bonds, *i.e.*, sharing two electrons.

Po does not form  $Po^{2-}$  anion. However, it forms  $Po^{2+}$  ions. Oxygen shows -2 oxidation state in its compounds except in oxygen fluorides. The tendency to show -2 oxidation state decreases as we go down in the group. However, positive oxidation states are exhibited by S, Se, Te and Po. In addition to +2 oxidation state +4 and +6 oxidation states are observed. This is due to availability of d-orbitals in these elements.

The compounds having +4 oxidation state show both oxidising and reducing properties while compounds having +6 oxidation state are only oxidising.

- All the elements of group 16 form hydrides of the type H<sub>2</sub>M. H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se, H<sub>2</sub>Te and H<sub>2</sub>Po.
  - (a) H<sub>2</sub>O is a liquid while other hydrides are colourless poisonous gases with bad odours. H<sub>2</sub>O (water) has low volatility (high boiling point) as hydrogen bonding is

- present. H<sub>2</sub>S has high volatility as no hydrogen bonding is present. Volatility decreases from H<sub>2</sub>S to H<sub>2</sub>Te due to increase in molecular masses.
- (b) As the electronegativity difference between M and H decreases, the covalent character increases from H<sub>2</sub>O to H<sub>2</sub>Te. Water is highly polar. It has high dielectric constant.
- (c) Thermal stability decreases. This is due to an increase in M—H bond length. Water dissociates at 2000°C while  $H_2$ Te decomposes at room temperature.
- (d) Acidic nature increases from H<sub>2</sub>O to H<sub>2</sub>Te.
- (e) Except H<sub>2</sub>O, other hydrides are reducing agents.
- (f) Hydrides of S, Se, Te and Po burn in oxygen with blue flame forming dioxides.
- (g) All these hydrides are V-shaped. The central atom is  $sp^3$  hybridized. The bond angles are 104.5°, 92.5°, 91° and 90° in H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se and H<sub>2</sub>Te.
- 7. S, Se, Te and Po form oxides on burning in air of the type  $MO_2$ , e.g.,  $SO_2$ ,  $SEO_2$ ,  $TEO_2$  and  $POO_2$ .

The acidic and stability of these oxides decrease down the group.  $SO_2$  and  $SeO_2$  are acidic while  $TeO_2$  and  $PoO_2$  are amphoteric.  $SO_2$  is a gas,  $SeO_2$  is a volatile solid while  $TeO_2$  and  $PoO_2$  are crystalline solids.  $SO_2$  is an angular molecule with bond angle 119.5°. S is in  $sp^2$  hybridized state. The bond length is 143 Å.

$$p\pi - d\pi$$
 bond  $p\pi - p\pi$  bond  $p\pi - p\pi$  bond

- S, Se and Te also form trioxides. The trioxides are acidic in nature. The acidic nature decreases from SO<sub>3</sub> to TeO<sub>3</sub>.
- 8. Sulphur, selenium and tellurium form similar oxyacids.

H <sub>2</sub> SO <sub>3</sub> Sulphurous acid Salts: Sulphites	H <sub>2</sub> SeO <sub>3</sub> Selenous acid Selenites	H <sub>2</sub> TeO <sub>3</sub> Tellurous acid Tellurites	increases
H <sub>2</sub> SO <sub>4</sub> Sulphuric acid Salts: Sulphates	H <sub>2</sub> SeO <sub>4</sub> Selenic acid Selenates	H <sub>2</sub> TeO <sub>4</sub> Telluric acid Tellurates	Strength in

Strength increases

9. S, Se and Te form hexafluorides of type MF<sub>6</sub>. They all involve sp<sup>3</sup>d<sup>2</sup> hybridization, i.e., possess octahedral structure. These are colourless gases. SF<sub>6</sub> is extremely inert. SeF<sub>6</sub> is slightly reactive while TeF<sub>6</sub> is hydrolysed by water into H<sub>6</sub>TeO<sub>6</sub>. Many tetrahalides are known. SF<sub>4</sub> is a gas, SeF<sub>4</sub> is a liquid while TeF<sub>4</sub> is a solid. S, Se, Te and Po form tetrachlorides and bromides while Te and Po form tetraiodides. All tetrahalides posses trigonal bipyramid structure with sp<sup>3</sup>d hybridization. One position is occupied by lone pair and four by halogen atoms.

All elements except Se form stable dichlorides and dibromides. Dihalides form tetrahedral molecules due to  $sp^3$  hybridization. Dimeric monohalides as  $S_2F_2$ ,  $S_2Cl_2$  and  $S_2Br_2$  are known. Their structures are similar to  $H_2O_2$ .

10. Only S and Se form oxyhalides. They are called thionyl and selenyl halides.

SOF<sub>2</sub> SOCl<sub>2</sub> SOBr<sub>2</sub> SeOF<sub>2</sub> SeOCl<sub>2</sub> SeOBr<sub>2</sub>

They react with water readily.

In addition, sulphuryl halides are also known,  $SO_2X_2$ . These may be regarded as derivatives of  $H_2SO_4$  where both the OH groups have been replaced by halogen atoms.

11. Lavoisier regarded oxygen as an essential constituent of all acids named it so (oxus = acid and gennas = maker). It occurs in the atmosphere to the extent of 21% by volume and 23% by mass. This percentage remains constant by the process of photosynthesis. It is an essential ingredient in all living matter and is of great importance in respiration and combustion.

It is a colourless, odourless and tasteless gas. It is little heavier than air and slightly soluble in water. It is paramagnetic in nature. There are three isotopes of oxygen with mass numbers 16, 17 and 18. Oxygen is not combustible but it helps in combustion. It is very active element. It directly combines with almost all metals (except noble metals) and non-metals (except zero group elements and halogens) and reacts with large number of compounds. The reactions are usually exothermic.

- 12. Oxygen combines nearly with all the elements except inert gases, noble metals and halogens. The binary compounds of oxygen with other elements are called oxides. However, the compounds of oxygen and fluorine are termed fluorides as fluorine is more electronegative than oxygen. The oxides can be classified, on the basis of chemical behaviour, into:
  - (a) Acidic oxides: The oxides which dissolve in water to form oxoacids are called acidic oxides or acid anhydrides. These react with bases and form salts. They also combine with basic oxides. These oxides are generally formed by non-metals. Examples are: CO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, NO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, N<sub>2</sub>O<sub>5</sub>, SO<sub>2</sub>, Cl<sub>2</sub>O<sub>7</sub>, etc. Some metals in higher oxidation states also form acidic oxides such as V<sub>2</sub>O<sub>5</sub>, CrO<sub>3</sub>, Mn<sub>2</sub>O<sub>7</sub>, etc. Some of the oxides form two oxyacids. These are called mixed oxides such as NO<sub>2</sub>, P<sub>4</sub>O<sub>3</sub>, etc.
  - (b) Basic oxides: The oxides which either dissolve in water to form alkalies or combine with acids to form salts or combine with acidic oxides are called basic oxides. The examples are Na<sub>2</sub>O, CaO, CuO, PbO, FeO, etc.
  - (c) Neutral oxides: The oxides which neither combine with acids nor combine with bases to form salts.

    Examples are: CO, N<sub>2</sub>O, H<sub>2</sub>O, NO, etc.
  - (d) Amphoteric oxides: The oxides which react with acids and bases both are termed amphoteric. Examples are: ZnO, PbO, SnO, SnO<sub>2</sub>, PbO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, BeO, Cr<sub>2</sub>O<sub>3</sub>, etc.

Oxides are also classified on the basis of oxygen content.

- (a) Normal oxides: These contain oxygen just as much as permitted by usual valence rules.
- **(b) Polyoxides:** These contain more oxygen than permitted by usual valence rules.

- (i) **Peroxides:** These on treatment evolve H<sub>2</sub>O<sub>2</sub> with dilute acids such as Na<sub>2</sub>O<sub>2</sub>, BaO<sub>2</sub>, etc.
- (ii) Superoxides: Such as MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>7</sub>, KO<sub>2</sub>, RbO<sub>2</sub>, etc.
- (c) Suboxides: These contain less oxygen permitted by usual valency rules such as N<sub>2</sub>O, CO, etc.
- (d) Mixed oxides: These are made up of two similar oxides such as Pb<sub>3</sub>O<sub>4</sub> (2PbO + PbO<sub>2</sub>), Fe<sub>3</sub>O<sub>4</sub> (Fe<sub>2</sub>O<sub>3</sub> + FeO), Mn<sub>3</sub>O<sub>4</sub> (2MnO + MnO<sub>2</sub>).
- 13. In 1840, Schonbien observed that rotten smell during passing of electric discharge through air was due to formation of a new gas which he named ozone (ozo = I smell). Sorret established its formula, O<sub>3</sub> and attributed that ozone is an allotrope of oxygen.

Ozone is present in sufficient amounts in the atmosphere at higher altitudes, *i.e.*, 12 to 15 miles above earth's surface. It is formed there by action of ultraviolet rays of the sun. Near earth's surface ozone is decomposed by dust particles.

It is obtained by passing silent electric discharge through dry oxygen. The apparatus used for this purpose is called **ozoniser**. The commonly used ozonisers are (i) Siemen's ozoniser and (ii) Brodie's ozoniser. The mixture obtained from ozoniser consists of 5–10% ozone by volume and the mixture is called **ozonised oxygen**. The ozonised oxygen is cooled by liquid air when liquid oxygen is obtained.

Fluorine reacts with water at low temperature when mixture of ozonised oxygen is formed.

14. Ozone is a pale blue gas with a characteristic strong smell. It can be liquefied to pale blue liquid at -112.4°C. It is heavier than air. It is slightly soluble in water but more soluble in turpentine oil, glacial acetic acid or carbon tetrachloride. It causes headache and nausea.

It is unstable and decomposes completely into oxygen at  $300^{\circ}$ C. It acts as a powerful oxidising agent. The potential equation is :  $O_3 \longrightarrow O_2 + O$ . The oxidation potential is + 2.07 V. It is a good bleaching agent. The bleaching action is due to its oxidising nature. It bleaches oil, ivory, flour, starch, waxes, pulp, etc.

It reacts with unsaturated organic compounds containing double bonds forming **ozonides**. The ozonides break with water to form carbonyl compounds. The process is known as **ozonolysis**. Mercury is oxidised by ozone to suboxide (Hg<sub>2</sub>O) which dissolve in mercury. It starts sticking to glass and loses mobility. The mercury loses its meniscus. This is termed as the **tailing of mercury**. Ozone molecule is V-shaped with a bond angle 116.8° and O—O bond length 1.278 Å.

- 15. The name sulphur has been derived from sanskrit word sulveri meaning killer of copper. It is widely distributed in nature both in free and combined state. The free sulphur is found in volcanic regions of the world. The underground sulphur is extracted by Frasch process.
- **16.** Organic compounds of plant and animal origin, *e.g.*, onion, garlic, mustard, eggs, proteins, hair, wool, etc., contain sulphur compounds.

- 17. Sulphur exists in several allotropic forms. The most common form is the rhombic or octahedral or  $\alpha$ -form. It is pale yellow in colour. Its specific gravity is 2.06. It melts at 114.5°C. It is insoluble in water and readily soluble in CS2. It consists S8 structural units packed together into octahedral shape. This is the stable variety at ordinary temperature. All other forms such as monoclinic, plastic sulphur, etc., are unstable and convert themselves into rhombic form.
- 18. Hydrogen sulphide or sulphureted hydrogen (H<sub>2</sub>S) occurs in volcanic gases, sewage gases, coal gas and in several spring waters. It is found in small amounts in atmosphere. It is obtained in the laboratory by the action of dilute H<sub>2</sub>SO<sub>4</sub> on FeS in kipp's apparatus. Pure H<sub>2</sub>S can be prepared by the action of pure HCl on antimony sulphide (Sb<sub>2</sub>S<sub>3</sub>).

It cannot be dried by conc. H<sub>2</sub>SO<sub>4</sub> because it is oxidised to sulphur.

$$H_2S + H_2SO_4 \longrightarrow 2H_2O + S + SO_2$$

It is, therefore, dried by passing through  $CaCl_2$  or  $P_2O_5$ . It is a colourless gas with unpleasant odour. It is slightly heavier than air and slightly soluble in water. It is poisonous in nature. It burns with blue flame in oxygen or air forming  $SO_2$  and  $H_2O$ . It acts as a strong reducing agent. It reacts with metals and metal oxides to form corresponding sulphides.  $H_2S$  reacts with salts of various metals forming corresponding sulphides. The metal sulphides can be divided into three groups:

- (a) Sulphides precipitated in acidic medium—Examples : Sulphides of Hg, Bi, Pb, Cu, Ag, Cd, As, Sb and Sn.
- (b) Sulphides precipitated in alkaline medium—Examples : Sulphides of Zn, Ni, Co, Mn and Fe.
- (c) Sulphides which are precipitated neither in acidic nor in alkaline medium—Examples: Sulphides of Cr, Al, Mg, Ba, Sr, Ca, K and Na.

The shape of  $H_2S$  molecule is similar to that of water, *i.e.*, V-shaped. The bond length is 1.35Å and bond angle 92.5°.

19. Sulphur forms a number of oxides such as S<sub>2</sub>O, SO, S<sub>2</sub>O<sub>3</sub>, SO<sub>2</sub>, SO<sub>3</sub>, S<sub>2</sub>O<sub>7</sub> and SO<sub>4</sub>. Out of these SO<sub>2</sub> and SO<sub>3</sub> are important and common.

 $SO_2$  is a colourless gas with pungent and suffocating odour. It is heavier than air. It is soluble in water. It neither burns nor helps in burning. However, burning Mg or K continue to burn in its atmosphere.

$$3Mg + SO_2 \longrightarrow 2MgO + MgS;$$
  
 $4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$ 

It is an acidic oxide. It dissolves in water forming sulphurous acid (H<sub>2</sub>SO<sub>3</sub>). It combines directly with chlorine to form sulphuryl chloride. It combines with oxygen in presence of a catalyst (platinised asbestos or V<sub>2</sub>O<sub>5</sub> or NO) when SO<sub>3</sub> is formed.

It acts as a reducing as well as an oxidising agent. In presence of moisture, it acts as a bleaching agent. The bleaching action is due to reduction. The bleaching is temporary.

20. A large number of oxyacids are known in the case of sulphur either in free state or in the form of salts or both. Oxyacids

with S—S links are called thioacids. Acids having sulphur in lower oxidation state belong to -ous series while those having sulphur in higher oxidation state belong to -ic series.

(a) Sulphurous acid (H<sub>2</sub>SO<sub>3</sub>): This acid is known only in solution. It is formed by passing SO<sub>2</sub> through water. It is a strong dibasic acid and forms two series of salts (i) bisulphites (e.g., NaHSO<sub>3</sub>) and (ii) sulphites (e.g., Na<sub>2</sub>SO<sub>3</sub>). The salts are fairly stable. The sulphurous acid, bisulphites and sulphites act as reducing agents. X-ray analysis of the crystal of Na<sub>2</sub>SO<sub>3</sub> has revealed that SO<sub>3</sub><sup>2-</sup> ion has a pyramidal structure. The S-atom is in sp<sup>3</sup> hybridized form, i.e., tetrahedral configuration in which

one position is occupied by a lone pair of electrons.

(b) Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>): It is considered as king of chemicals. The prosperity of any country is measured by the amount of sulphuric acid it consumes. It was called in ancient days *oil of vitriol* as it was obtained by distilling ferrous sulphate (green vitriol). Native sulphur is the starting material for its preparation. It is burnt and is easily converted into SO<sub>2</sub>. The conversion of SO<sub>2</sub> into SO<sub>3</sub> is bit difficult. It requires a catalyst. The trioxide dissolves in water to form H<sub>2</sub>SO<sub>4</sub>.

$$S \longrightarrow SO_2 \longrightarrow SO_3 \longrightarrow H_2SO_4$$

Two processes are used for the manufacture of H<sub>2</sub>SO<sub>4</sub>.

- (i) Lead chamber process: In this process, the mixture containing SO<sub>2</sub>, air and NO when treated with steam, sulphuric acid is formed. NO is a catalyst. The acid obtained contains about 80% H<sub>2</sub>SO<sub>4</sub> and is known as brown oil of vitriol (B.O.V.) due to its colour. It can be further concentrated and the concentrated acid is called rectified oil of vitriol (R.O.V.). Usually chamber acid is not purified and used as such for most<sub>2</sub> of the purposes.
- (ii) Contact process: The process involves the conversion of SO<sub>2</sub> into SO<sub>3</sub> by air in presence of a catalyst (platinum or V<sub>2</sub>O<sub>5</sub>). Best results are obtained when SO<sub>2</sub> and O<sub>2</sub> are present in molecular proportion of 2:3. The optimum temperature is 450°C. The purification of gases is very necessary in this process. The SO<sub>3</sub> formed is absorbed in conc. H<sub>2</sub>SO<sub>4</sub> when oleum is formed. SO<sub>3</sub> cannot be absorbed in water because it produces a dense fog. The acid obtained is pure.

H<sub>2</sub>SO<sub>4</sub> is a colourless syrupy liquid. It contains 98.3% H<sub>2</sub>SO<sub>4</sub>. Its specific gravity is 1.84 at 15°C. It fumes strongly in moist air and highly corrosive in nature. It is highly soluble in water. Various hydrates such as H<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>·3H<sub>2</sub>O,

H<sub>2</sub>SO<sub>4</sub>·4H<sub>2</sub>O are known. Heat is evolved when dissolved in water. Water should not be added to conc. H<sub>2</sub>SO<sub>4</sub> for dilution but conc. H<sub>2</sub>SO<sub>4</sub> should be added slowly to cold water with constant stirring. Due to its great affinity for water, it is used as dehydrating agent. Its corrosive action on skin is due to dehydration. It boils at 338°C. It is a conductor of heat and electricity.

 $H_2SO_4$  is a strong dibasic acid. It forms two series of salts (i) bisulphates (e.g., NaHSO<sub>4</sub>) and (ii) sulphates (e.g., Na<sub>2</sub>SO<sub>4</sub>). It acts as a strong oxidising agent. The potential equation is:  $H_2SO_4 \longrightarrow H_2O + SO_2 + O$  or  $2H_2SO_4 + 2e \longrightarrow SO_4^{2-} + 2H_2O + SO_2$ . It has two OH groups which are directly attached to sulphur. The acid is a resonance hybrid of the following two structures.

 $SO_4^{2-}$  ion has tetrahedral structure, *i.e.*, S is in  $sp^3$  hybridization.

- (c) Thiosulphuric acid (H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>): It is a dibasic acid. It does not exist in free state. Salts are quite stable. Thiosulphates are reducing agents.
- (d) Peroxymonosulphuric acid or Caro's acid (H<sub>2</sub>SO<sub>5</sub>): It is a dibasic stable and crystalline solid. It has a peroxolinkage OHOOH. It is a strong oxidising agent.
- (e) Peroxydisulphuric acid or Marshall's acid (H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>): It is a dibasic acid. It has a peroxolinkage. It is a strong oxidising agent.

(f) Dilhionic acid (H<sub>2</sub>S<sub>2</sub>O<sub>6</sub>): It is a dibasic acid. It does not exist in free state but its salts are quite stable.

- 21. The IUPAC name of  $H_2S$  is sulphane.
- 22. (a) SF<sub>6</sub> is used in high voltage transformers because of its insulating property.
  - (b) Liquid oxygen mixed with finely divided carbon is used in place of dynamite in coal mining.
  - (c) A mixture of ozone and cyanogen is used as a rocket fuel.
  - (d) Gun powder is a mixture of sulphur, charcoal and KNO<sub>3</sub>.

- (e) S<sub>2</sub>Cl<sub>2</sub> is used in the vulcanisation of rubber.
- (f) Electrical conductivity of Se is negligible in dark but increases on exposure to light. Due to this property, Se is used in photo electric cells.
- 23. The chemical reactions of ozone with oxides of nitrogen and with chlorofluoro-alkanes are responsible for the depletion

of ozone shield of the atmosphere. This is called 'ozone hole'. It is feared that this will allow an excessive amount of UV light to reach the earth which will cause **melanoma** (skin cancer) in humans.

# -•••- PRACTICE PROBLEMS -•••-

### ■ Subjective Type Questions

- 1. Name the elements of group 16 which have:
  - (i) highest electronegativity
  - (ii) maximum ionisation enthalpy
  - (iii) highest catenation property
  - (iv) highest electropositive nature.
- 2. Among the hydrides of group 16 elements, which have :
  - (i) lowest boiling point
  - (ii) highest bond angle
  - (iii) maximum acidic nature
  - (iv) neutral in nature.
- 3. List the elements O, S, Se and Te in the order of decreasing: (i) boiling point (ii) electronegativity (iii) ionisation energy.
- 4. Sulphuric acid acts as an acid, an oxidising agent and as a dehydrating agent. In which way does it behave when it acts on:
  - (a) Glucose, (b) Sulphur, (c) Calcium carbonate, (d) Copper,
  - (e) Formic acid, (f) Hydrogen iodide, (g) Sodium hydroxide,
  - (h) Carbon.
- 5. What happens when?
  - Hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide.
  - (ii) Hydrogen sulphide is passed through acidified ferric chloride solution.
  - (iii) Sulphur is boiled with caustic soda solution.
  - (iv) Ozone reacts with potassium ferrocyanide solution.
  - (v) Ozone is treated with ethylene. [M.L.N.R. 1990]
  - (vi) Sulphur dioxide is bubbled through aqueous solution of copper sulphate in presence of potassium thiocyanate.
  - (vii) Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride.
  - (viii) Sulphuric acid is treated with PCl<sub>5</sub>.
  - (ix) Ozone is passed through acidified stannous chloride solution.
  - (x) Potassium iodide is heated with conc. H<sub>2</sub>SO<sub>4</sub>.
- 6. Complete the following equations:
  - (i)  $(NH_4)_2S_2O_8 + H_2O + MnSO_4 \longrightarrow \dots + \dots + \dots$

[I.I.T. 1993]

(ii) 
$$S + H_2SO_4(conc.) \xrightarrow{Heat} \dots + H_2O$$

(iii) 
$$I_2 + SO_2 + H_2O \longrightarrow SO_4^{2-} + \dots + H^+$$

(iv) 
$$I_2 + O_3 + H_2O \longrightarrow HIO_3 + \dots$$

(v) 
$$Cr_2O_7^{2-} + H^+ + SO_2 \longrightarrow SO_4^{2-} + H_2O + \dots$$

- (vi)  $H_2S + HNO_3 \longrightarrow \dots + H_2O + S$  (Colloidal)
- (vii)  $Fe^{2+} + SO_3^{2-} + H^+ \longrightarrow Fe^{3+} + H_2O + S$
- (viii)  $Mn^{2+} + S_2O_8^{2-} + H_2O \longrightarrow MnO_4^- + H^+ + SO_4^{2-}$
- (ix)  $MnO_4^- + H_2S \longrightarrow S + Mn^{2+} + H_2O$  (Acidic medium)
- 7. From the reactions given below, identify (A), (B), (C) and (D) and their formulae.
  - (A) + dil.  $H_2SO_4$  +  $K_2Cr_2O_7$   $\longrightarrow$  (B) Green coloured

$$(A) + \text{dil. } H_2SO_4 + (C) \longrightarrow MnSO_4$$

$$(A) + O_2 \xrightarrow{H_2O} (D)$$
  
 $(D) + BaCl_2 \longrightarrow White ppt.$ 

- 8. Arrange the following:
  - (a) H<sub>2</sub>S, H<sub>2</sub>O, H<sub>2</sub>Se, H<sub>2</sub>Te in order of increasing acidity.
  - (b) H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se, H<sub>2</sub>Te in order of increasing stability.
  - (c) H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub> in order of decreasing acidity.
  - (d) Po, Se, Te, S, O in order of increasing metallic properties.
  - (e) Po, Se, Te, S, O in order of decreasing ionisation potential.
- 9. Give at least one example to explain the following properties:
  - (i) Sulphuric acid is a dibasic acid.
  - (ii) Sulphuric acid is a dehydrating agent.
  - (iii) Conc. H<sub>2</sub>SO<sub>4</sub> acts as an oxidising agent.
  - (iv) H<sub>2</sub>S acts as a reducing agent.
  - (v) SO<sub>2</sub> acts as a reducing agent.
  - (vi) SO<sub>3</sub> is an acid anhydride of H<sub>2</sub>SO<sub>4</sub>.
- 10. A mixture of three gases A, B and C is passed first through acidified  $K_2Cr_2O_7$  solution when A is absorbed turning  $K_2Cr_2O_7$  solution green. Remainder is passed through excess of lime water which turns milky resulting in absorption of B. The residual gas C is absorbed in alkaline pyrogallol solution. The mixture of A; B and C does not turn lead acetate paper black. Identify A, B and C.
- 11. Answer the following:
  - (i) Write the general electronic configuration of VIA or 16th group.
  - (ii) Name two chalcogens.
  - (iii) Which element of VIA group has maximum catenation property?
  - (iv) Name the hydride of VIA group elements which is liquid at room temperature.
  - (v) Which allotropic form of sulphur is more stable at room temperature?

- (vi) Which gas is formed in the upper layers of atmosphere by action of UV radiations?
- (vii) The common oxidation states of VIA group elements are . . . . . .
- (viii) What is the other name of peroxy disulphuric acid?
- (ix) Name the acid used in storage batteries.
- (x) What is the reason for the syrupy nature of conc. H<sub>2</sub>SO<sub>4</sub>?
- (xi) Among the hydrides, H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se, which has the highest bond angle?
- (xii) Write the formula of oleum.
- (xiii) Which catalyst is used in the manufacture of H<sub>2</sub>SO<sub>4</sub> by contact process? [M.L.N.R. 1997]
- (xiv) What are the most favourable conditions of temperature and pressure for the conversion of  $SO_2$  into  $SO_3$ ?
- (xv) The other name of sulphuric acid is . . . . . .
- 12. Write the hybridization state of the central atom, shape and electronic structure of the following molecules or ions.
  - (i) Sulphur trioxide,
- (iv) Sulphate ion
- (ii) Sulphuric acid,
- (v) Ozone
- (iii) Sulphur dioxide,
- (vi) Hydrogen sulphide
- 13. Explain the following:
  - (i) Oxygen is a gas while sulphur is a solid.

[Ans. The oxygen molecule is diatomic involving a double bond. Its small size produces weak intermolecular forces amongst its molecules and is, thus, a gas at room temperature. Sulphur is incapable of forming  $\pi$ -bonds. Its molecule has a puckered ring structure of eight sulphur atoms joined by single covalent bonds. The intermolecular forces acting between  $S_8$  molecules are stronger and hence, sulphur is a solid.]

(ii) Water is liquid while H<sub>2</sub>S is a gas.

to form a cluster.

[Ans. Oxygen is more electronegative than sulphur. Thus, oxygen can form hydrogen bonds. Water is an associated liquid due to hydrogen bonding. The hydrogen bonding is absent in H<sub>2</sub>S, hence the molecules are unassociated. It, therefore, exists in gaseous state.]

(iii) Sulphuric acid has high boiling point and viscosity.
 [Ans. The high boiling point and viscous nature of conc.
 H<sub>2</sub>SO<sub>4</sub> is due to hydrogen bonding due to which a number of sulphuric acid molecules are associated

(iv) Oxygen almost invariably exhibits an oxidation state of -2 but the other members of the family exhibit negative as well as positive oxidation states of +2, +4 and +6.

[Ans. All the elements of oxygen family have a configuration of  $ns^2$   $np^4$  of the outermost orbit. They all tend to attain 8 electrons by accepting two more electrons, *i.e.*, all show -2 oxidation state. Oxygen has no d-orbitals while, others have d-orbitals in their valency shells. Thus, the paired

orbitals can be unpaired by shifting electrons to d-orbitals.

+4	ns	np	nd	
Ground state	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\uparrow$		+2 oxidation state
1st excited state	$\uparrow$	$\boxed{\uparrow   \uparrow   \uparrow}$	$\uparrow$	+4 oxidation state
2nd excited state	$\uparrow$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\uparrow \uparrow \uparrow$	+6 oxidation state

The elements of oxygen family except oxygen, therefore, show +2, +4 and +6 oxidation states besides -2.]

(v) The tendency to show -2 oxidation state diminishes from sulphur to polonium.

[Ans. On moving down the group, the size of the atom increases and the electronegativity decreases. Thus, the tendency to accept two more electrons as to attain octet in outermost shell decreases, i.e., the tendency to show -2 oxidation state decreases.]

(vi) Sulphur dioxide is more powerful reducing agent in an alkaline medium than in acidic medium. [I.I.T. 1992]

[Ans. The reducing property is represented as,

$$SO_2 + 2OH^- \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

Addition of acid favours reverse reaction whereas presence of OH<sup>-</sup> favours the forward reaction.]

(vii) Dry SO<sub>2</sub> does not bleach dry flowers.

[Ans. Only in presence of moisture, the nascent hydrogen responsible for bleaching (reduction) is produced.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$
  
Coloured flower + H  $\longrightarrow$  Colourless flower ]

(viii) H<sub>2</sub>S is stronger acid than H<sub>2</sub>O.

[Ans. The H—S bond is weaker than H—O bond and the proton is more easily released when H<sub>2</sub>S reacts with water.]

(ix) Hydrogen sulphide cannot be dried by passing through conc. H<sub>2</sub>SO<sub>4</sub>.

[Ans. Conc. H<sub>2</sub>SO<sub>4</sub> is an oxidising agent while H<sub>2</sub>S is a reducing agent. Both react to form free sulphur.]

(x) Nitric acid cannot be used to prepare  $H_2S$ . [Ans. Nitric acid is an oxidising agent. It will oxidise  $H_2S$ .  $3H_2S + 2HNO_3 \longrightarrow 2NO + 3S + 4H_2O$ 

(xi) In the manufacture of sulphuric acid by the contact process, sulphur trioxide is not directly dissolved in water.

[Ans.  $SO_3$  reacts with water to form  $H_2SO_4$  which is not easily condensed and escapes in the atmosphere. It is, therefore, absorbed in conc.  $H_2SO_4$  to form oleum which may be diluted to form  $H_2SO_4$ .

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$
  
 $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$ 

(xii) For the dilution of H<sub>2</sub>SO<sub>4</sub>, water should not be added to conc. H<sub>2</sub>SO<sub>4</sub>.

[Ans. Conc. H<sub>2</sub>SO<sub>4</sub> has great affinity for water molecules.

During addition of water, large amount of heat energy is released. The temperature rises suddenly and bumping takes place. To avoid any accident, acid

should be added to water with constant stirring rather than water to acid.]

(xiii) Conc. H<sub>2</sub>SO<sub>4</sub> cannot be used for drying H<sub>2</sub>. [Ans. Hydrogen, sometimes, ignites with the large amount of heat released when water is absorbed by acid.]

(xiv) The bond angle in  $H_2S$  is lower than in  $H_2O$ .

[Ans. S is less electronegative than oxygen. The bonded electrons in H<sub>2</sub>S move further away from S-atom than O-atom in H2O. This decreases repulsion between bonded electrons and thus, there is contraction in bond angle.]

(xv) KMnO<sub>4</sub> should not be dissolved in conc. H<sub>2</sub>SO<sub>4</sub>. [Ans. Mn<sub>2</sub>O<sub>7</sub> is formed which is unstable and explosive in nature.

$$2KMnO_4 + 2H_2SO_4 \longrightarrow K_2SO_4 + (MnO_3)_2SO_4 + 2H_2O$$
  
 $(MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4$ 

(xvi) Ozone layer in the upper regions of atmosphere protects earth from the harmful radiations of sun.

> [Ans. Harmful UV radiations are emitted by sun. The ozone layer is capable of absorbing these radiations and thus protects the earth from these radiations.]

- 14. An aqueous solution of a gas (X) gives the following reactions:
  - (i) It decolourizes an acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution.
  - On boiling with H<sub>2</sub>O<sub>2</sub>, cooling it and then adding an aqueous solution of BaCl<sub>2</sub>, a precipitate insoluble in dil. HCl is obtained.
  - (iii) On passing H<sub>2</sub>S in the solution, white turbidity is obtained. Identify (X) and give equations for steps (i), (ii) and (iii). [Roorkee 1993]

[Hint: Step (iii) suggests that 
$$(X)$$
 is  $SO_2$ .

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$
Turbidity

(i) 
$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$
  
Colourless solution

(ii) 
$$\begin{array}{ccc} H_2O_2 + SO_2 & \longrightarrow & H_2SO_4 \\ H_2SO_4 + BaCl_2 & \longrightarrow & BaSO_4 + 2HCl \ ] \\ & & & White ppt. \end{array}$$

15. A pale yellow substance (A) when heated with conc. HNO<sub>3</sub> evolves a brown coloured gas (B). The substance (A) also dissolves in sodium sulphite solution on heating. A clear solution (C) is formed which on acidification gives a turbid solution and a pungent smelled gas (D) which is formed by the substance (A) in air. The solution (C) decolourises iodide solution. Identify (A) to (D).

[Hint: Substance (A) is sulphur.

$$\begin{array}{c} S + 6HNO_3 \longrightarrow H_2SO_4 + 2H_2O + 6NO_2 \\ (A) & (B) \\ S + Na_2SO_3 \longrightarrow Na_2S_2O_3 \\ (A) & (C) \\ Na_2S_2O_3 + H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + S + H_2O \\ (C) & (D) \text{ Turbidity} \\ 2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI ] \\ (C) & \text{Colourless solution} \end{array}$$

16. An inorganic halide (A) reacts with water to form two acids (B) and (C). (A) also reacts with NaOH to form two salts (D) and (E) which remain in solution. The solution gives white precipitates with both AgNO3 and BaCl2 solutions respectively. (A) is a useful organic reagent. [Hint:  $A = SO_2Cl_2$ 

$$SO_2Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

$$(A) \qquad (B) \qquad (C)$$

$$SO_2Cl_2 + 4KOH \longrightarrow K_2SO_4 + 2KCl + 2H_2O$$

$$(A) \qquad (D) \qquad (E)$$

$$BaCl_2 \qquad AgNO_3$$

$$BaSO_4 \qquad AgCl \qquad ]$$
Whiteppt. Whiteppt.

17. In the contact process for industrial manufacture of sulphuric acid some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the [LLT. 1999] oxidation of SO<sub>2</sub>?

### Matching Type Questions

### Match the following:

[A] (a) Oleum

(i) NO·HSO<sub>4</sub>

(b) Peroxy disulphuric acid

(ii) H<sub>2</sub>SO<sub>5</sub>

(c) Peroxy monosulphuric acid

(iii) H<sub>2</sub>SO<sub>3</sub>

Chamber crystals

(iv)  $H_2S_2O_7$ 

Sulphurous acid

(v)  $H_2S_2O_8$ 

[B] (i) Sulphur dioxide

(a) Laboratory reagent for mixture analysis

(ii) Oxygen

(b) Oleum

(iii) Ozone

(c) Vulcanizing rubber

(iv) Hydrogen sulphide

(d) Petroleum refining

(v) Sulphur

(vi) Sulphuric acid

(e) Paramagnetic

Marshall's acid

(vii) Fuming sulphuric acid

(g) Antichlor

(viii) Peroxy disulphuric acid (h) Detection of double

bond in organic compounds.

## Answers

### **Answers**: Subjective Type Questions

- 1. (i) oxygen (ii) oxygen (iii) sulphur (iv) polonium or ununhexium
- 2. (i)  $H_2S$  (ii)  $H_2O$  (iii)  $H_2Te$  or  $H_2Po$  (iv)  $H_2O$
- 3. (i) Te > Se > S > O
  - (ii) O > S > Se > Te
  - (iii) O > S > Se > Te
- 4. (a) dehydrating agent, (b) oxidising agent, (c) an acid, (d) oxidising agent, (e) dehydrating agent, (f) oxidising agent, (g) an acid, (h) oxidising agent.
- 5. (i) (Moist)  $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$ 
  - (ii)  $2\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$
  - (iii)  $4S + 6NaOH \longrightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

Excess sulphur Na<sub>2</sub>S<sub>5</sub>

(iv)  $2K_4Fe(CN)_6 + O_3 + H_2O \longrightarrow 2K_3Fe(CN)_6 + 2KOH + O_2$ 

$$(v) \qquad CH_2 = CH_2 + O_3 \longrightarrow CH_2 \qquad CH_2$$

$$O \longrightarrow O$$

(vi)  $2CuSO_4 + SO_2 + 2KCNS + 2H_2O \longrightarrow$ 

 $2CuCNS + K_2SO_4 + 2H_2SO_4$ 

(vii)  $2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4$  $2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$ 

(viii)  $H_2SO_4 + 2PCl_5 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$ 

- (ix)  $3\operatorname{SnCl}_2 + 6\operatorname{HCl} + \operatorname{O}_3 \longrightarrow 3\operatorname{SnCl}_4 + 3\operatorname{H}_2\operatorname{O}$
- (x)  $2KI + H_2SO_4 \longrightarrow K_2SO_4 + 2HI$

 $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$ 

6. (i)  $(NH_4)_2S_2O_8 + H_2O \longrightarrow (NH_4)_2SO_4 + H_2SO_4 + O$  $MnSO_4 + H_2O + O \longrightarrow MnO_2 + H_2SO_4$ 

### $(NH_4)_2S_2O_8 + MnSO_4 + 2H_2O \longrightarrow (NH_4)_2SO_4 + MnO_2 + 2H_2SO_4$

- (ii)  $S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$
- (iii)  $I_2 + SO_2 + 2H_2O \longrightarrow SO_4^{2+} + 2I^- + 4H^+$
- (iv)  $I_2 + 5O_3 + H_2O \longrightarrow 2HIO_3 + 5O_2$
- (v)  $Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 3SO_4^{2-} + H_2O + 2Cr^{3+}$
- (vi)  $H_2S + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + S$  (colloidal)
- (vii)  $4Fe^{2+} + SO_3^{2-} + 6H^+ \longrightarrow 4Fe^{3+} + S + 3H_2O$
- (viii)  $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^{-} + 16H^{+} + 10SO_4^{2-}$
- $(ix) \quad 2MnO_4^- + 6H^+ + 6H_2S \longrightarrow 2Mn^{2+} + 5S + 8H_2O$
- 7.  $(A) = \text{Na}_2\text{SO}_3$ ;  $(B) = \text{Cr}_2(\text{SO}_4)_3$ ;  $(C) = \text{KMnO}_4$ ;  $(D) = \text{Na}_2\text{SO}_4$
- 8. (a)  $H_2O < H_2S < H_2Se < H_2Te$ 
  - (b)  $H_2Te < H_2Se < H_2S < H_2O$
  - (c)  $SO_3 > N_2O_5 > CO_2 > SiO_2 > H_2O$
  - (d) O < S < Se < Te < Po
  - (e) O > S > Se > Te > Po
- (i) One molecule of H<sub>2</sub>SO<sub>4</sub> consists two replaceable hydrogen atoms and forms two series of salts.

NaOH + H<sub>2</sub>SO<sub>4</sub> 
$$\longrightarrow$$
 NaHSO<sub>4</sub> + H<sub>2</sub>O

Sodium hydrogen
sulphate (acidic salt)

$$\begin{array}{ccc} 2NaOH + H_2SO_4 & \longrightarrow & Na_2SO_4 & + \ 2H_2O \\ & & \text{Sodium sulphate} \\ & & \text{(normal salt)} \end{array}$$

(ii) H<sub>2</sub>SO<sub>4</sub> has great affinity for water molecules, and hence it acts as a dehydrating agent.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$
Sugar
$$C_{arbon} + 11H_2O$$

$$C_{arbon} + 11H_2O$$

$$C_{arbon} + 11H_2O$$

(iii) H<sub>2</sub>SO<sub>4</sub> oxidises metals, non-metals and other compounds. Sulphur in H<sub>2</sub>SO<sub>4</sub> is in +6 oxidation state, thus it can change into-lower-oxidation-states, *i.e.*, +4, -2, etc.

Cu + 
$$2H_2SO_4$$
 (conc.)  $\longrightarrow$  CuSO<sub>4</sub> + SO<sub>2</sub> +  $2H_2O$   
 $2P + 5H_2SO_4 \longrightarrow 2H_3PO_4 + 2H_2O + 5SO_2$   
 $2HBr + H_2SO_4 \longrightarrow SO_2 + Br_2 + 2H_2O$ 

(iv) Sulphur in  $H_2S$  is in -2 oxidation state, thus it can increase the oxidation state only and hence it acts as a reducing agent.

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$
  
 $H_2S + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + S$ 

(v) As it can be oxidised to sulphuric acid, it acts as a reducing agent.

$$SO_2 \longrightarrow H_2SO_4$$

$$O.N. +4 +6$$

$$Cl_2 + 2H_2O + SO_2 \longrightarrow H_2SO_4 + 2HCl$$

$$2FeCl_3 + 2H_2O + SO_2 \longrightarrow H_2SO_4 + 2FeCl_2 + H_2SO_4$$

(vi) SO<sub>3</sub> combines with water to form H<sub>2</sub>SO<sub>4</sub>, hence it is an acid anhydride of H<sub>2</sub>SO<sub>4</sub>.

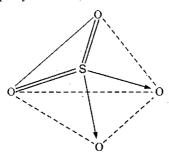
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

- **10.** A is SO<sub>2</sub> as it turns acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution green. (It is not H<sub>2</sub>S as it does not turn lead acetate paper black.) B is CO<sub>2</sub> as it turns lime water milky and C is oxygen which is absorbed in alkaline pyrogallol.
- 11. (i)  $ns^2 np^4$ , (ii) Oxygen and sulphur, (iii) Sulphur, (iv) Water, H<sub>2</sub>O, (v) Rhombic, (vi) Ozone, (vii) -2, +2, +4, +6, (viii) Marshall acid, (ix) H<sub>2</sub>SO<sub>4</sub>, (x) Intermolecular hydrogen bonding, (xi) H<sub>2</sub>O,
  - (xii) H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, (xiii) Platinised asbestos or vanadium pentoxide, (xiv) Low temperature (optimum temperature 450°C) and high pressure (optimum pressure 2 to 3 atmospheres), (xv) Oil of vitriol.
- 12. (i)  $SO_3$ ,  $sp^2$  hybridization, planar triangular

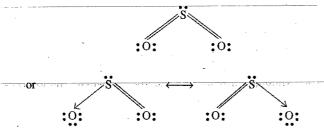


The equivalence of all S—O bonds suggest that  $SO_3$  is a resonance hybrid of the following structures :

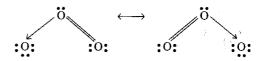
(ii) H<sub>2</sub>SO<sub>4</sub>, sp<sup>3</sup> hybridization, tetrahedral



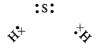
(iii) SO<sub>2</sub>, sp<sup>2</sup> hybridization, V-shaped



(iv) O<sub>3</sub>, sp<sup>2</sup> hybridization, angular (V-shaped)



(v) H<sub>2</sub>S, sp<sup>3</sup> hybridization, V-shaped



Answers: Matching Type Questions

## ILLUSTRATIONS OF OBJECTIVE QUESTIONS



- 1. Concentrated H<sub>2</sub>SO<sub>4</sub> can be used to dry the gas:
  - (a) H<sub>2</sub>S

(b) CO<sub>2</sub>

(c) NH<sub>3</sub>

(d) all

Ans. (b)

[Hint: H<sub>2</sub>S and NH<sub>3</sub> react with H<sub>2</sub>SO<sub>4</sub> while CO<sub>2</sub> is not affected.

- 2. Sulphur on reaction with concentrated HNO<sub>3</sub> gives (A) which reacts with NaOH gives (B). (A) and (B) are:
  - (a) H<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>
- (b) NO2, Na2S
- (c) H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>
- (d)  $H_2S_2O_3$ ,  $Na_2S_2O_3$

Ans. (c)

Hint:

$$6 \text{HNO}_3 + \text{S} \longrightarrow \text{H}_2 \text{SO}_4 + 6 \text{NO}_2 + 2 \text{H}_2 \text{O} \; ;$$
 
$$(A) \\ \text{H}_2 \text{SO}_4 + 2 \text{NaOH} \longrightarrow \text{Na}_2 \text{SO}_4 + 2 \text{H}_2 \text{O} \; ]$$
 
$$(B)$$

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$
(B)

- 3. The structures of  $O_3$  and  $N_3^-$  are:
  - (a) linear and bent respectively
  - (b) both linear
  - (c) both bent
  - (d) bent and linear respectively

Ans. (d)

- 4. When an inorganic compound reacts with SO<sub>2</sub> in aqueous medium produces (A). (A) on reaction with Na<sub>2</sub>CO<sub>3</sub> gives the compound (B) which with sulphur gives a substance (C) used in photography. The compound (C) is:
  - Ans. (a)
  - (a)  $Na_2S_2O_3$  (b)  $Na_2SO_4$  (c)  $Na_2S$

[Hint:  $Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2$ 

(d) Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub>

$$2NaHSO_3 + Na_2CO_3 \longrightarrow 2Na_2SO_3 + H_2O + CO_2$$

$$(B)$$

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

$$(C)$$

- 5. Acidified KMnO<sub>4</sub> is dropped over sodium peroxide taken in a flask at room temperature, vigorous reaction takes place to produce:
  - (a) hydrogen peroxide
  - (b) a mixture of hydrogen and oxygen
  - (c) a colourless gas hydrogen
  - (d) a colourless gas dioxygen

Ans. (d)

[Hint: 
$$[Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2] \times 5$$
  
 $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$   
 $[H_2O_2 + O \longrightarrow H_2O + O_2] \times 5$ 

$$2KMnO_4 + 8H_2SO_4 + 5Na_2O_2 \longrightarrow 5Na_2SO_4 + K_2SO_4 + 2MnSO_4 \\ + 8H_2O + 5O_2]$$

Among the oxides given below which are acidic?

CrO<sub>3</sub>, Mn<sub>2</sub>O<sub>7</sub>, CuO, CO, SO<sub>2</sub>

- (a) Only SO<sub>2</sub>
- (b) CrO<sub>3</sub>, Mn<sub>2</sub>O<sub>7</sub> and SO<sub>2</sub>
- (c) Mn<sub>2</sub>O<sub>7</sub> and SO<sub>2</sub>
- (d) CO and SO<sub>2</sub>

Ans. (b)

[Hint: 
$$CrO_3 + H_2O \longrightarrow H_2CrO_4$$
;  
 $Mn_2O_7 + H_2O \longrightarrow 2HMnO_4$ ;  
 $SO_2 + H_2O \longrightarrow H_2SO_3$ 

CuO is a basic oxide while CO is a neutral oxide.]

- 7. In which of the following reactions  $O_2$  is not formed as one of the product?
  - (a) KClO<sub>3</sub> MnO<sub>2</sub> Heat

- (b)  $SnCl_2 + HCl + O_3 \longrightarrow$
- (c)  $FeSO_4 + H_2SO_4 + O_3 \longrightarrow$
- (d) PbS +  $O_3 \longrightarrow$

Ans. (b)

[Hint:  $3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$ ]

- **8.** The formation of which of the substance is known as tailing of mercury?
  - (a) Hg<sub>2</sub>O
- (b) HgO
- (c)  $Hg(NO_3)_2$
- (d) HgS

- Ans. (a)
- 9. Which of the following elements forms  $p\pi$ - $d\pi$  bonding in its oxide?
  - (a) Lithium
- (b) Boron
- (c) Sulphur
- (d) Nitrogen

Ans. (c)

[Hint: Among the given elements, sulphur forms  $d\pi$ - $p\pi$  bonding in its oxides such as SO<sub>2</sub> and SO<sub>3</sub>.]

10. In which of the following species, S-atom assumes sp<sup>3</sup> hybrid state?

 $I(SO_3); II(SO_2); III(H_2S); IV(S_8)$ 

(a) I, II

- (b) II, III
- (c) II, IV

(d) III, IV

Ans: (d)

- 11. Which of the following chemical reactions depicts the oxidising behaviour of H<sub>2</sub>SO<sub>4</sub>? [A.I.E.E.E. 2006]
  - (a)  $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
  - (b)  $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$
  - (c)  $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
  - (d)  $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

Ans. (a)

[Hint: In reaction (a), the O.N. of S reduces from +6 to +4.]

- **12.** The number of unpaired electrons in a paramagnetic diatomic molecule of an element with atomic number 16 is:
  - (a) 4

(b) 1

(c) 2

(d) 3

Ans. (c)

[Hint: S<sub>2</sub> molecule is paramagnetic like O<sub>2</sub> having 2 unpaired electrons.]

13. The molecular formula of dithionic acid is:

[C.E.T. (J&K) 2006]

- (a)  $H_2S_2O_4$
- (b)  $H_2S_2O_6$
- (c)  $H_2S_2O_5$
- (d)  $H_2S_2O_8$

Ans. (b)

14. Which among the following statements are correct?

### [P.E.T. (Kerala) 2007]

- (i) Carbon monoxide is neutral whereas SO3 is acidic
- (ii) Potassium oxide is basic whereas nitrous oxide is acidic
- (iii) Aluminium and zinc oxides are amphoteric
- (iv) Sulphur trioxide is acidic whereas phosphorus pentoxide is basic
- (v) Carbon dioxide is neutral whereas sulphur dioxide is amphoteric
- (a) (ii) and (iii)
- (b) (i) and (iv)
- (c) (i) and (iii)
- (d) (ii) and (iv)
- (e) (iii) and (v)
- Ans. (c)
- 15. Ozone is used for purifying water because: [C.P.M.T. 2007]
  - (a) it dissociates and release oxygen
  - (b) it does not leave any foul smell like chlorine
  - (c) it kills bacteria, cyst, fungi and acts as a biocide
  - (d) all of the above

Ans. (d)

## **OBJECTIVE QUESTIONS**



			- 11 V II.		<u>. The control of the second s</u>			
Set	I: This set contains que	estions with one correct a	nswe	er.	•			
1.	The formula of sulphur mo	lecule is:		14.	The number of unpaired	elect	rons in the $p$ -subshell of $\nabla$	VΙΑ
	(a) $S_2$	☐ (b) S <sub>4</sub>			or 16th group of the period	odic	table is:	
	(c) $S_6$	$\square$ (d) $S_8$			(a) 1		(b) 2	
2.	The most stable allotropic	form of sulphur is:			(c) 3		(d) 4	
	(a) rhombic	(b) monoclinic		15.	Which shows maximum of	cater	nation property?	
	(c) plastic	☐ (d) milk of sulphur			(a) Te		(b) Se	
3.	Ozone is:	_			(c) S		(d) O	
	(a) compound of oxygen			16.	Ozone readily dissolves i	n:		
	(b) allotrope of oxygen				(a) H <sub>2</sub> O		(b) CS <sub>2</sub>	
	(c) isotope of oxygen	-			(c) turpentine oil		(d) ammonia	
	(d) mixture of atomic and r	nolecular oxygen		17.	The maximum bond angle	is i	and the second s	
4.		n ozonised oxygen is about:			(a) H <sub>2</sub> O		(b) H <sub>2</sub> S	
	(a) 40	- <del>-</del>		ļ	(c) H <sub>2</sub> Se	Д.	Carana morales de la caración de la	
	• •	□ (d) 100		18.	Which one of the metal	sticl	ks to glass plate on treatn	nent
5.	The product A in the follow	wing equation:			with ozone?			
	<del>-</del>	$+ MnO_2 + O_2$ , is:			(a) Silver		(b) Mercury	
					(c) Copper		` '	
				19.	Moist iodine reacts with	ozon		_
6.	. , 2	$ClO_3$ in the preparation of oxy	gen		(a) HI		(b) $I_2O_5$	
		ature of KClO <sub>3</sub> is reduced f			(c) $HIO_3$		(d) HIO <sub>4</sub>	
	350°C to			20.	In the laboratory H <sub>2</sub> S is			_
	_	□ (b) 150°C			- · ·		(b) dilute H <sub>2</sub> SO <sub>4</sub> on FeSO	$\bigcirc_3 \square$
	• •	☐ (d) room temperature			(c) hydrogen on sulphur			Ц
7.		g heating evolves oxygen is:		21.	When H <sub>2</sub> S is passed throu	igh a	acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solution	, the
		$\square$ (b) $Al_2O_3$			solution turns:			_
	·       =	☐ (d) BaO <sub>2</sub>		1	(a) yellow		(b) blue	닏
8.	Non-metals combine with				(c) white	. 🗆	(d) green	
-		☐ (b) neutral oxides		22.	Which one of the follow			_
		☐ (d) amphoteric oxides			(a) Hydrogen sulphide			
9.	Which one of the followin			20	(c) Sulphur dioxide		(d) Ozone	
		(b) ZnO		23.	-	nea	by the action of dilute $H_2$	304
	· ,	□ (d) CO <sub>2</sub>			on:		71) P 11.	_
10.	In the upper layers of atm	· · · · -			(a) copper turning		(b) sodium sulphate	니
		ischarge on oxygen molecule	s 🗆		(c) sodium sulphite		(d) sodium sulphide	
		t rays on oxygen molecules		24.	The formula of oleum is:			
	(c) by action of infrared r				(a) $H_2SO_5$		(b) $H_2S_2O_7$	
	(d) due to sudden drop of				(c) $H_2S_2O_3$		(d) $H_2S_2O_8$	
11.	On heating ozone, its volu	ime:		25.	Low volatile nature of H	_		
	(a) increases to $1\frac{1}{2}$ times	☐ (b) decreases to half			(a) strong bonds		(b) hydrogen bonding	
	(c) remains unchanged				(c) van der Waals' force		· ·	
12.	Which requires catalyst?			26.	The ratio of the gases of	otain	ed on dehydration of HCC	OOH
		$\Box \text{ (b) } 2SO_2 + O_2 \longrightarrow 2SO$	, 🗆		and H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> by conc. H <sub>2</sub>	$SO_4$	is:	
	(c) $C + O_2 \longrightarrow CO_2$				(a) 2:1		(b) 1:2	
13.	In the reaction,	· ,			(c) 3:1		(d) 1:3	
•		$\longrightarrow$ 2KOH + O <sub>2</sub> + A,			[Hint: HCOOH—H <sub>2</sub> SO <sub>4</sub>	→CO	+H <sub>2</sub> O;	
	the compound $A$ is:				$H_2C_2O_4$ $H_2SO_4$		=	
		□ (b) I <sub>2</sub> O <sub>5</sub>			The ratio is $1:2$ .		1 CO2 T H2O	
		☐ (d) I <sub>2</sub>			ine iduo is 1 . 2.			
	\-/ <b>-</b> /	\-/- \-/-\-		1				

27.	Which one of the following on heating will give mixture of	of		0 0	
	SO <sub>2</sub> and SO <sub>3</sub> ?				
	(a) $ZnSO_3$ $\square$ (b) $CuSO_4$	]  .		[Hint: HO — S — S — OH]	
	(c) $Na_2SO_4$	]		0	
28.	Which of the following oxides is amphoteric in character?	'	39.	Which is the most basic of the following oxides?	
	[A.I.E.E.E. 2005			(a) Na <sub>2</sub> O	
		<u> </u>		(c) $ZnO$ $\Box$ (d) $P_2O_3$	
•				Which of the following is the most acidic?	_
29.	Ozone molecule is:	_		(a) Al <sub>2</sub> O <sub>3</sub>	
				(c) $MgO$ $\Box$ (d) $CaO$	
	and the contract of the contra	<b>5</b> 1		Which is not the characteristic of conc. H <sub>2</sub> SO <sub>4</sub> ?	_
20		_		(a) Oxidising agent	
30.	Which of the following hydrides of the oxygen family show	78	•	(c) Hygroscopic	
	the lowest boiling point?	<u>-</u>	42.	H <sub>2</sub> S is passed through potassium permanganate solution,	
		]	72.	get:	WC
	(-)2	<b>-</b>		(a) potassium sulphide $\Box$ (b) sulphur	П
31.	A considerable part of the harmful ultraviolet radiation of the			(c) potassium sulphite	
	sun does not reach the surface of earth. This is because it	in	43.		ч.
	the upper atmosphere, there is a layer of:			The gas O <sub>3</sub> cannot oxidise: (a) KMnO <sub>4</sub>	
	(a) $O_3$ $\square$ (b) $CO_2$	□			
	(c) $NH_3$ $\square$ (d) $H_2$	<b>_</b>	11	(c) KI	
32.	SF <sub>6</sub> is unreactive towards water because:	ŀ	44.	Which statement about H <sub>2</sub> S is false?	П
	(a) sulphur has very small size			(a) It is a covalent compound	
	(b) fluorine is most electronegative element			(b) It is a gas with bad smell	
	- · · · · · · · · · · · · · · · · · · ·			(c) It is a weak base in water	
	(d) due to steric hindrance water molecule cannot attac	k	15	(d) It is a stronger reducing agent	ш
	S-atom		45.	Sulphur does not exist as $S_2$ molecule because :	$\Box$
33.	In sulphate ion the oxidation state of sulphur is +6 ar	nd		(a) It is less electronegative	
	hybridization state of sulphur is:			(b) It has ability to exhibit catenation	
				(c) It is not able to constitute $p\pi$ - $p\pi$ bond	
	, , ,		16	(d) It has the tendency to show variable oxidation state	
34.	The catalyst used in the manufacture of sulphuric acid by	- 1	46.	The gases respectively absorbed by alkaline pyrogallol	and
.J-1.	lead chamber process is:	, y		oil of cinnamon is:	П
				(a) $O_3$ , $CH_4$	
			APT.	(c) $O_2$ , $O_3$	
25	· · · - ·	_	47.	Ordinary oxygen contains:	_
33.	From the following information	\		(a) a mixture of $O^{16}$ , $O^{17}$ and $O^{18}$	ᆜ
	$X + H_2SO_4 \longrightarrow Y$ (a colourless and irritating ga	is)		(b) a mixture of $O^{16}$ and $O^{17}$	
	$Y + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$ green coloured solution	l		(c) only O <sup>16</sup>	
	Identify the pair $X$ and $Y$ .	_	40	(d) only O <sup>18</sup>	
			48.	Anhydride of sulphuric acid is:	P3
	(-) - ,2-			(a) $SO_2$ $\square$ (b) $SO_3$	
36.	The catalyst used in the manufacture of H <sub>2</sub> SO <sub>4</sub> by conta	ict		(c) $H_2S_2O_3$ $\square$ (d) $H_2SO_3$	
	process is:		49.	Sulphuric acid is a dibasic acid in nature, hence it forms	s:
				(a) acidic salt $\Box$ (b) acidic and basic salt	
	(c) Fe			(c) acidic and normal salt \( \square\) (d) double salt	
37.	Oleum is:		50.	When SO <sub>2</sub> is passed through a solution of H <sub>2</sub> S in water	r:
	(a) a mixture of conc. H <sub>2</sub> SO <sub>4</sub> and oil			(a) sulphuric acid is formed	
	(b) sulphuric acid saturated with SO <sub>3</sub>			(b) a clear solution is formed	
				(c) sulphur is precipitated	
				(d) no change is observed	
38.		on	51.	Conc. H <sub>2</sub> SO <sub>4</sub> displaces hydrogen chloride from chloride	ides
	states of sulphur can be:			because:	
				(a) it is stronger than hydrochloric acid	
	(a) 15 and 12	_		(b) HCl is a gas while H <sub>2</sub> SO <sub>4</sub> is a liquid	

	( )1	2	66.	Caro's acid is:	_	
				(a) $H_2SO_5$	$\square$ (b) H <sub>2</sub> SO <sub>3</sub>	
52.	The valency of sulphur in $SO_4^{2-}$ is:	1		(c) $H_3S_2O_5$	$\square$ (d) $H_2S_2O_8$	
	(a) 2 $\square$ (b) 1		67.	Marshall's acid is:		
	(c) 4			(a) $H_2S_2O_5$	$\square$ (b) $H_2S_2O_8$	
53.	$SO_2 + H_2S \longrightarrow Product$ . The final product is:			(c) $H_2SO_5$	$\square$ (d) H <sub>2</sub> SO <sub>4</sub>	
	[J.E.E. (Orissa) 200	5]	68.	Ozone turns benzidine pa	aper:	
	(a) $H_2SO_4$			(a) violet	☐ (b) brown	
	(c) $H_2S_2O_3$			(c) blue	☐ (d) red	
54.	An element forms a gaseous oxide which on dissolving	in	69.	SO <sub>2</sub> is:	•	
	water gives an acidic solution. The element is:	1		(a) acidic	☐ (b) alkaline	
				(c) neutral	☐ (d) amphoteric	
		口。	70	Which one of the follow	ring_statements_is_wrong?	
55.	Fuming sulphuric acid is:			(a) H <sub>2</sub> S is a dibasic acid		
				(b) H <sub>2</sub> S acts only as a re	educing agent	
				(c) The bond angle in H2	<sub>2</sub> S is 109°28′	
56.	Which of the following turns lead acetate paper black?			(d) H <sub>2</sub> S has rotten smell		
			71.	Which one of the follow	ring statements is wrong?	
				(a) SO <sub>2</sub> dissolves in wat	ter and forms sulphurous aci	d 📮
57.	What is same in various hydrides of chalcogens?	1		(b) SO <sub>2</sub> acts as a bleach	ing agent	
	·			(c) SO <sub>2</sub> has pungent od	our	
				(d) SO <sub>2</sub> acts only as oxi	dising agent	
	· ·		72.	About H <sub>2</sub> SO <sub>4</sub> , which of the	he following statements is inc	orrect?
				(a) It acts as a reducing	agent	
58.	Which of the following elements occurs in native state?			(b) It acts as an oxidisin	ng agent	
	and the second s			(c) It acts as dehydratin	g agent	
	(c) Si			(d) It is highly viscous		
59.	When concentrated H <sub>2</sub> SO <sub>4</sub> is added to dry KNO <sub>3</sub> , brow	vn	73.	Which one of the follow	ring is wrong?	
	fumes evolve. These fumes are of:			(a) Oxygen and sulphur l	belong to the same group of p	eriodic
	(a) $SO_2$ $\square$ (b) $SO_3$	□.		table	•	
	(c) $NO_2$		•	(b) Oxygen is a gas whi	le sulphur is solid	
60.	Mark the wrong statement. When Na <sub>2</sub> S is added to sodiu	ım		(c) Both show $+2$ , $+4$ ar		
	nitroprusside solution:			(d) H <sub>2</sub> S has no hydroge		
			74.	Which one of the follow		
	(-)			(a) PbO <sub>2</sub>	$\square$ (b) BaO <sub>2</sub>	
	1 2 73 3			(c) $Na_2O_2$	$\square$ (d) $H_2O_2$	
			75.		g oxides exists as trigonal	
61.	When H <sub>2</sub> S is passed through nitric acid solution, the produ	ıct		•	ite and a cyclic trimer in th	e solid
	formed is:			state?	•	
	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \			(a) $SO_2$	$\square$ (b) SeO <sub>2</sub>	
				(c) $SeO_3$	$\square$ (d) SO <sub>3</sub>	
62.	Mark the compound which gives carbon with conc. H <sub>2</sub> SC	) <sub>4</sub> :	76.	Which of the following	acts as pickling agent?	
	* * * * * * * * * * * * * * * * * * * *				[C.P.M.]	r. <b>200</b> 6]
	``			(a) HNO <sub>3</sub>	$\Box$ (b) H <sub>2</sub> SO <sub>4</sub>	
63.	70			(c) HCl	$\square$ (d) HNO <sub>2</sub>	
	•		77.	H <sub>2</sub> S is far more volatile		
	· / 1 · · ·			(a) sulphur atom is mor	e electronegative than oxyge	n atom
	(c) heating with a cobalt salt					Ц
	· · · · · · · · · · · · · · · · · · ·			(b) oxygen atom is mor	e electronegative than sulphi	ır atom
64.	Ozone reacts with K <sub>4</sub> Fe(CN) <sub>6</sub> to form:		1			
	(a) $Fe_2O_3$			(c) H <sub>2</sub> O has bond angle	•	
<b>بد</b> بر.	( ) 5 ( ) 2	Ц	-		oosely bonded with sulphur	, . 🗆
65.	· · ·	_	78.		s an oxidising as well as a re	educing
	(a) reduction			agent?		. —
	(c) its acidic nature			(a) $SO_2$	$\Box  \text{(b) MnO}_2$	· 📙
	•		I	(c) $Al_2O_3$	$\square$ (d) CrO <sub>3</sub>	

79.	When SO <sub>2</sub> is passed through cupric chloride solution:	(a) three $\Box$ (b) two $\Box$
	(a) the solution becomes colourless and a white ppt. of	(c) one $\Box$ (d) zero $\Box$
	$Cu_2Cl_2$ is obtained	92. In OF <sub>2</sub> molecule, the total number of bond pairs and lone
	(b) a white ppt. is obtained	pairs of electrons present respectively are: [D.P.M.T. 2002]
	(c) the solution becomes colourless	(a) 2,6 $\Box$ (b) 2,8 $\Box$
,	(d) no visible change takes place	(c) 2, 10 $\Box$ (d) 2, 9 $\Box$
80.	The acid used in lead storage cells is:	93. Which of the following has $p\pi$ - $d\pi$ bonding?
	(a) phosphoric acid $\Box$ (b) nitric acid $\Box$	[C.B.S.E. 2002]
	(c) hydrochloric acid	(a) $NO_3^-$
81.	Hydrolysis of one mole of peroxydisulphuric acid produces:	(c) $BO_3^{3-}$
	(a) two moles of sulphuric acid $\Box$	94. In the species $O_2$ , $O_2^+$ , $O_2^-$ and $O_2^{2-}$ , the correct decreasing
	(b) two moles of peroxymonosulphuric acid $\Box$	order of bond strength is: [A.I.E.E.E. 2002]
	(c) one mole of sulphuric acid and one mole of peroxy-	(a) $O_2 > O_2^+ > O_2^- > O_2^2$
	monosulphuric acid	1
	(d) one mole of sulphuric acid, one mole of peroxymono-	(b) $O_2^+ > O_2 > O_2^- > O_2^2$
	sulphuric acid and one mole of hydrogen peroxide	(c) $O_2^{2-} > O_2^{-} > O_2^{+} > O_2$
82.	Which of the following bonds has the highest energy?	(d) $O_2^- > O_2^{2-} > O_2 > O_2^+$
	(a) Se—Se	95. The angular shape of ozone molecule (O <sub>3</sub> ) consists of:
92		[C.B.S.E. 2008]
83.	permanent dipole moment?	(a) 1 sigma and 1 pi bond
	<u> </u>	(b) 2 sigma and 1 pi bond
	(a) $H_2S$ $\square$ (b) $SO_2$ $\square$ (c) $SO_3$ $\square$ (d) $CS_2$ $\square$	(c) 1 sigma and 2 pi bonds
84.	Which of the following is the most powerful oxidising agent?	(d) 2 sigma and 2 pi bonds  96. Excess of PCl <sub>5</sub> reacts with conc. H <sub>2</sub> SO <sub>4</sub> giving:
04.	(a) $H_2SO_4$ $\Box$ (b) $H_3BO_3$ $\Box$	[C.E.T. (Karnataka) 2008]
	(c) HPO <sub>3</sub> $\square$ (d) H <sub>3</sub> PO <sub>4</sub> $\square$	(a) sulphuryl chloride  (b) sulphurous acid
85.	3	(c) chlorosulphonic acid (d) thionyl chloride
	state?	97. The element evolving two different gases on reaction with
	(i) $SO_3$ (ii) $H_2S$ (iii) $CS_2$ (iv) $S_8$	conc. H <sub>2</sub> SO <sub>4</sub> is: [P.E.T. (Kerala) 2008]
	(a) (i) and (ii) $\square$ (b) (ii) and (iii) $\square$	(a) P
	(c) (ii) and (iv) $\square$ (d) (iii) and (iv) $\square$	(c) Hg $\Box$ (d) S $\Box$
86.		(e) Sn
	(a) non-metals	98. Select the incorrect statement about the following:
	(c) radioactive $\Box$ (d) polymorphic $\Box$	[J.E.E. (W.B.) 2008]
87.	The geometry of H <sub>2</sub> S and its dipole moment are:	(a) $O_3$ is used as germicide for purification of air
	(a) angular and non-zero □ (b) angular and zero □	(b) In O <sub>3</sub> , O—O bond length is identical with that of
	(c) linear and zero $\Box$ (d) linear and non-zero $\Box$	molecular oxygen
88.	The oxidation number of sulphur in S <sub>8</sub> , S <sub>2</sub> F <sub>2</sub> , H <sub>2</sub> S respec-	(c) O <sub>3</sub> molecule is angular in shape
	tively, are:	(d) O <sub>3</sub> is an oxidising agent
	(a) $0, +1 \text{ and } -2$	99. The correct order of O—O bond length in O <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> and O <sub>3</sub>
	(c) $0, +1 \text{ and } +2$ $\square$ (d) $-2, +1 \text{ and } -2$ $\square$	is: [P.E.T. (Rajasthan) 2006] (a) $O_3 > H_2O_2 > O_2$ $\Box$ (b) $O_2 > H_2O_2 > O_3$ $\Box$
89.	Which of the following does not have S—S linkage?	(a) $O_3 > H_2O_2 > O_2$
	[Roorkee (S) 2000]	100. In which of the following ions, there is no S—S bond?
	(a) $S_2O_8^{2-}$	[P.M.T. (Kerala) 2008]
	(c) $S_2O_5^{2-}$	(a) $S_2O_4^{2-}$
90.	Amongst $H_2O$ , $H_2S$ , $H_2Se$ and $H_2Te$ , the one with highest	(c) $S_2O_2^{2-}$
- 0.	boiling point is: [I.I.T. (S) 2000]	(c) $S_2O_2$
	(a) H <sub>2</sub> O because of hydrogen bonding	
	(b) H <sub>2</sub> Te because of higher molecular weight	
	(c) H <sub>2</sub> S because of hydrogen bonding	(a) $3O_2 = 2O_2$ : $\Delta H = -284.5 \text{ kJ}$
	(d) H <sub>2</sub> Se because of lower molecular weight	(a) $3O_2 \rightleftharpoons 2O_3$ ; $\Delta H = -284.5 \text{ kJ}$
91.	The number of S—S bonds in sulphur trioxide trimer S <sub>3</sub> O <sub>9</sub>	(b) ozone undergoes addition reaction with unsaturated
	is: [I.I.T. (S) 2001]	carbon compounds

102.	tetrathionate and sodi (d) ozone oxidises lead s The number of sigma and are, respectively: (a) 9 and 4 (c) 4 and 8 [Hint: Structure peroxydis	ium sulph pi be	aide to lead sulphate onds in peroxydisulphuric [E.A.M.C.E.T. (Engg.) 2 (b) 11 and 4 (d) 4 and 9 uric acid $ \begin{array}{c c} O & O & S & O & H \\ \hline O & O & O & S & O & H \\ \hline O & O & O & O & O & O & O & O & O \\ \hline O & O & O & O & O & O & O & O & O & O &$	acid 2008]		The function of Fe(OH)  (a) to detect colloidal im (b) to remove moisture (c) to remove dust partic (d) to remove arsenic im  wers.	purit	[C.E.T. (Karnataka) y	<b>2006</b> ]
	Which among the follow				_	Select the correct statem	ents	about Na <sub>2</sub> S <sub>2</sub> O <sub>2</sub> ·5H <sub>2</sub> O:	
	(a) H <sub>2</sub> SO <sub>3</sub>	Ď	-			(a) It is also called as h			
	(c) $H_2S_2O_8$		$(d)$ $H_2SO_4$			(b) It is used in photogra		to form complex with A	gBr□
105.		ents	about oxygen molecule:	man and timing operation / districts		(c) It can be used as an			
	(a) It is paramagnetic					(d) It is used to remove	stain	s of I <sub>2</sub>	
	(b) Its bond order is two	)			110.	Which of the following	are a	mphoteric?	
	(c) In liquid state it is bl	lue c	oloured			(a) BeO		(b) $Al_2O_3$	
	(d) It has two unpaired	elect	rons			(c) ZnO		(d) SO <sub>2</sub>	
106.	SO <sub>2</sub> acts as:				111.		-	-	roduct
	(a) bleaching agent		(b) oxidising agent			during oxidation with ox	zone?		
	(c) reducing agent		(d) disinfectant			(a) $SO_2$		(b) SnCl <sub>2</sub> /HCl	
107.	Sulphuric acid can be us			_	مند	(c) H <sub>2</sub> S		(d) PbS	
	(a) hygroscopic agent		(b) oxidising agent		112.	In which of the following	_	-	<u></u>
100	(c) sulphonating agent		(d) efflorescent			(a) Caro's acid		(b) Dithionic acid	
108.	H <sub>2</sub> S can be used as:	<b>,1</b>	(h) h	_	112	(c) Thiosulphuric acid		(d) Chlorosulphonic a	.cid L
	(a) acid		(b) base		113.	Peroxo acids of sulphur		(L) II 00	_
	(c) oxidising agent		(d) reducing agent		ŀ	(a) $H_2SO_4$		(b) H <sub>2</sub> SO <sub>3</sub>	
					1	(c) H <sub>2</sub> SO <sub>5</sub>	· 🖂	(d) H <sub>2</sub> S <sub>2</sub> O <sub>2</sub>	

1.	(d)	2.	(a)	3.	(b)	4.	(c)	5.	(b)	6.	(c)	7.	(d)	8.	(c)	9.	(b)	10.	(b)
11.	(a)	12.	(b)	13.	(d)	14.	(b)	15.	(c)	16.	(c)	17.	(a)	18.		19.	(c)	20.	(a)
21.	(d)	22.	(a)	23.	(c)	24.	(b)	25.	(b)	26.	(b)	27.	(d)	28.	(d)	29.	(b)	30.	(b)
31.	(a)	32.	(d)	33.	(d)	34.	(c)	35.	(b)	36.	(a)	37.	(b)	38.	(c)	39.	(a)	40.	(a)
41.	(b)	42.	(b)	43.	(a)	44.	(c)	45.	(c)	46.	(c)	47.	(a)	48.	(b)	49.	(c)	50.	(c)
51.	(b)	<b>52.</b>	(d)	53.	(d)	54.	(c) *	55.	(d)	56.	(d)	57.	(a)	58.	(b)	59.	(c)	60.	(c)
61.	(b)	62,	(d)	63.	(c)	64.	(d)	65.	(a)	66.	(a)	67.	(b)	68.	(b)	69.	(a)	70.	(c)
71.	(d)	72.	(a)	73.	(c)	74.	(a)	<b>75.</b>	(d)	76.	(b)	77.	(b)	78.	(a)	<b>79.</b>	(a)	80.	(d)
81.	(c)	82.	(c)	83.	(d)	84.	(a)	85.	(c)	86.	(d)	87.	(a)	88.	(a)	89.	(a)	90.	(a)
91.	(d)	92.	(b)	93.	(b)	94.	(b) .	95.	(b)	96.	(a)	97.	(b)	98.	(b)	99.	(d)	100.	(e)
101.	(a)	102.	(b)	103.	(d)	104.	(b, c)	105.	(a,b,c,d)	106.	(a,b,c,d)	107.	(a,b,c)	108.	(a,d)	109.	(a,b,c,d)	110.	(a,b,c
111.	(a,b)	112.	(b,c)	113.	(c,d)														



## Objective Questions for IIT ASPIRANTS



- 1. When sulphur is boiled with Na<sub>2</sub>SO<sub>3</sub>, a compound (A) is produced. (A) with excess of AgNO3 solution gives a compound (B) which is water soluble and produces a black coloured sulphide (C). Compounds (A), (B) and (C) will be respectively:
  - (a) Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Ag<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Ag<sub>2</sub>S
  - (b) Na<sub>2</sub>SO<sub>4</sub>, Ag<sub>2</sub>SO<sub>4</sub>, Ag<sub>2</sub>S
  - (c) Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, Ag<sub>2</sub>SO<sub>4</sub>, Ag<sub>2</sub>S
  - (d) Na<sub>2</sub>SO<sub>5</sub>, Ag<sub>2</sub>SO<sub>5</sub>, Ag<sub>2</sub>SO<sub>4</sub>

[Hint: 
$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$
;  
 $Na_2S_2O_3 + 2AgNO_3 \longrightarrow 2NaNO_3 + Ag_2S_2O_3$ ;  
 $Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$ ]

- 2. An organic acid (A) reacts with concentrated H<sub>2</sub>SO<sub>4</sub> to give a neutral oxide (B), acidic oxide (C) and a diatomic oxide (D). When (D) reacts with chlorine gas, a poisonous gas (E) is evolved. This gas with ammonia gives an organic compound (F). The compounds (A) and (F) are:
  - (a)  $(A) = H_2C_2O_4$  and  $(F) = NH_2CONH_2$
  - (b)  $(A) = CH_3COOH$  and  $(F) = NH_2CONH_2$
  - (c)  $(A) = CHCl_3$  and  $(F) = H_2C_2O_4$
  - (d)  $(A) = CCl_4$  and  $(F) = CH_3CHO$

$$[ \text{Hint} : (COOH)_2 \xrightarrow{Conc. H_2SO_4} H_2O + CO_2 + CO \\ (A) & (B) & (C) & (D) \\ Neutral & Acidic & Diatomic oxide \\ CO + Cl_2 \longrightarrow COCl_2 \xrightarrow{NH_3} NH_2CONH_2 ] \\ (E) & (F) \\ Poisonous$$

- 3. Compounds A and B are treated with dilute HCl separately. The gases liberated are Y and Z respectively. Y turns acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> paper green while Z turns lead acetate paper black. The compounds A and B are respectively:
  - (a) Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub>
- (b) Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S
- (c) NaCl and Na<sub>2</sub>CO<sub>3</sub>
- (d) Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>

[Hint: SO<sub>2</sub> turns acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> paper green.

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + H_2O_4$$

 $K_2 Cr_2 O_7 + H_2 SO_4 + 3SO_2 \longrightarrow Cr_2 (SO_4)_3 + K_2 SO_4 + H_2 O$ 

 $H_2S$  turns lead acetate paper black.

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$$

$$H_2S + Pb(CH_3COO)_2 \longrightarrow PbS + 2CH_3COOH_3$$

- 4. A yellow coloured crystalline substance gave a colourless gas X on reaction with fluorine, which is thermally stable and has octahedral geometry. X can be:
  - (a)  $SF_4$

(c)  $SF_6$ 

- (d)  $S_2F_6$
- The number of lone pairs and the number of S—S bonds in S<sub>8</sub> molecules are respectively:

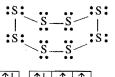
(a) 8,8

(b) 16,8

(c) 8, 16

(d) 8, 4

[Hint:  $S_8$  molecule is shown here. Every sulphur atom is in  $sp^3$ hybridized state.



 $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow$   $\uparrow$ 

Thus, there are 8 S-S bonds and 16 lone pairs.]

- 6. Tailing of mercury test can be used for which of the following gas?
  - (a) Dioxygen
- (b) Dihydrogen
- (c) Dinitrogen
- (d) Ozone
- Which of the following solutions does not change its colour on passing ozone through it?
  - (a) Starch iodide solution
  - (b) Alcoholic solution of benzidine
  - (c) Acidic solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
  - (d) Acidified solution of FeSO<sub>4</sub>

[Hint: Ozone does not react with acidified solution of  $K_2Cr_2O_7$ .]

- 8. A green coloured solution of a salt changes its colour to light pink on passing ozone through it. Which of the following species represent pink and green colour respectively?
  - (a) Mn<sup>2+</sup> and MnO<sub>2</sub> (c) Co<sup>2+</sup> and Co<sup>3+</sup>
    - (b)  $MnO_4^-$  and  $MnO_4^{2-}$ (d)  $MnO_4^{2-}$  and  $MnO_4^{-}$

[Hint: MnO<sub>4</sub><sup>2-</sup> is green while MnO<sub>4</sub><sup>-</sup> is pink. Ozone oxidises  $MnO_4^{2-}$  to  $MnO_4^{-}$ .

- 9. An oxide of a non-metal has the following properties:
  - (i) acts both as a proton donor as well as proton acceptor
  - (ii) it reacts readily with basic and acidic oxides
  - (iii) it oxidises Fe at its boiling point.

The oxide is:

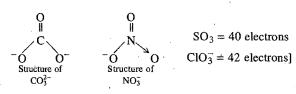
(a)  $P_2O_5$ 

(b) SiO<sub>2</sub>

(c) H<sub>2</sub>O

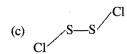
- (d) CO<sub>2</sub>
- 10. Oxygen is more electronegative than sulphur, yet H<sub>2</sub>S is acidic in nature while H<sub>2</sub>O is neutral because:
  - (a) water molecules are associated due to intermolecular hydrogen bonding
  - (b) water has higher boiling point than H<sub>2</sub>S
  - (c) H—S is weaker than O—H bond
  - (d) H<sub>2</sub>S is a gas at ordinary temperature while H<sub>2</sub>O is a liquid
- 11. Which of the following are isoelectronic and isostructural?
  - (a)  $NO_3^-, CO_3^{2-}$
- (b) SO<sub>3</sub>, NO<sub>3</sub><sup>-</sup> (d) CO<sub>3</sub><sup>2-</sup>, SO<sub>3</sub>
- (c)  $ClO_3^-, CO_3^{2-}$

[Hint:  $NO_3^-$  and  $CO_3^{2-}$  both have same number of electrons (32) electrons) and central atom in each being sp<sup>2</sup> hybridized.



- 12. O<sub>3</sub> cannot oxidise:
  - (a) KI
- (b) FeSO<sub>4</sub>
- (c) KMnO<sub>4</sub>
- (d)  $K_2MnO_4$
- 13. Which of the following is/are correct?
  - (a)  $O_3$  + moist iodine  $\longrightarrow$  HIO<sub>3</sub>
  - (b)  $FeCl_3 + H_2S \longrightarrow colloidal sulphur$
  - (c)  $O_3 + Ag \longrightarrow black silver$
- 14. A black sulphide when treated with ozone becomes white. The white compound is:
  - (a) ZnSO<sub>4</sub>
- (b) PbSO<sub>4</sub>
- (c) BaSO<sub>4</sub>
- (d) CaSO<sub>4</sub>
- [Hint: PbS  $\xrightarrow{O_3}$  PbSO<sub>4</sub>]
- White 15. Which of the following is correct structure of S<sub>2</sub>Cl<sub>2</sub>?

(a) 
$$S = S < \frac{Cl}{Cl}$$



- 16. What is the hybrid state and oxidation state of sulphur in Caro's acid?
  - (a)  $sp^2$ , +10 (c)  $sp^2$ , +6

[Hint: The structure of Caro's acid is

HO—S—O—O—H. The hybrid state is 
$$sp^3$$
 and its O

O.N. is +6.

- 17. Identify the correct sequence of increasing number of  $\pi$ -bonds in structures of the following molecules.
  - (i)  $H_2S_2O_6$  (ii)  $H_2SO_3$  (iii)  $H_2S_2O_5$
  - (a) I, II, III
- (b) II, III, I
- (c) II, I, III
- (d) I, III, II

$$H_2SO_3$$
, HO—S—OH—one π-bond;

- **18.** Sulphur reacts with chlorine in 1:2 ratio and forms (X). (X)on hydrolysis gives a sulphur compound (Y). What is the hybridized state of central atom in the anion of (Y)?
  - (a) sp (c) sp<sup>2</sup>

(b)  $sp^3$ 

[Hint:  $S + 2Cl_2 \longrightarrow SCl_4$ ;

$$\begin{array}{c} SCl_4 + 4H_2O \longrightarrow & S(OH)_4 + 4HCl \\ \downarrow \\ & H_2SO_3 + H_2O \\ (Y) \end{array}$$

The hybridized state of S in (Y) is  $sp^3$ .

9. (c)

- **1.** (a)
- 2. (a)
- 3. (b)
- **4.** (c)
- **5.** (b)
- 6. (d)
- 7. (c)
- 8. (d)
- 10. (c)

11. (a)

12. (c)

13. (d) 17. (b) 15. (c) 16. (d) 18. (b)

# **Assertion-Reason Type Questions**

The following questions consist of two statements as Assertion (A) and Reason (R). Examine the statements and answer the questions according to following instructions:

Mark (a) if both (A) and (R) are correct and (R) is the correct explanation of (A).

Mark (b) if both (A) and (R) are correct but (R) is not the correct explanation of (A).

Mark (c) if (A) is correct but (R) is wrong.

- Mark (d) if (A) is wrong but (R) is correct.
- Mark (e) if both (A) and (R) are wrong.

- 1. (A) Tailing of mercury occurs on passing O<sub>3</sub> through it.
  - (R) This is due to oxidation of mercury. [A.I.I.M.S. 1999]
- 2. (A) H<sub>2</sub>O is the only hydride of the chalcogens which is
  - (R) In ice, each O atom is surrounded by 4H atoms.
- 3. (A) Ozone is a powerful oxidising agent in comparison to
  - (R) Ozone is diamagnetic while O<sub>2</sub> is paramagnetic.

[A.I.I.M.S. 2005]

- 4. (A) SeCl<sub>4</sub> does not have a tetrahedral structure.
  - (R) Se in SeCl<sub>4</sub> has two lone pairs.
- [A.I.I.M.S. 2005]

- 5. (A) H<sub>2</sub>SO<sub>4</sub> forms only one series of salts.
  - (R) The molecule of H<sub>2</sub>SO<sub>4</sub> consists of only one OH group.
- 6. (A) SO<sub>3</sub> acts as an oxidising as well as a reducing agent.
  - (R) SO<sub>2</sub> acts as an oxidising as well as a reducing agent.

## Answers

**1.** (a)

**2.** (b)

**3.** (b)

4. (c)

**5.** (e)

**6.** (d)

# THOUGHT TYPE QUESTIONS

### **THOUGHT 1**

Sulphuric acid is considered as the king of chemicals. The prosperity of any country is measured by the amount of sulphuric acid it consumes. Sulphuric acid is, thus, a substance of very great commercial importance as it is used practically in every important industry. This is due to the following properties of sulphuric acid:

- (a)-acidic-nature
- (b) oxidising nature
- (c) dehydrating nature
- (d) sulphonation
- 1. Sulphuric acid has very corrosive action on skin because:
  - (a) it reacts with proteins
  - (b) it acts as an oxidising agent
  - (c) it acts as a dehydrating agent
  - (d) it acts as a dehydrating agent and absorption of water is highly exothermic.
- 2. Which of the following reactions depict the oxidising behaviour of  $H_2SO_4$ ?
  - (a)  $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
  - (b)  $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
  - (c)  $2\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
  - (d)  $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$
- 3. Sulphuric acid is used:
  - (a) in lead storage batteries (b) in making fertilizers
  - (c) in making explosives
- (d) in all of these
- **4.** The formation of nitroglycerine is done by the use of concentrated nitric acid and concentrated sulphuric acid. The process of conversion of glycerine into nitroglycerine is termed as:
  - (a) sulphonation
- (b) oxidation
- (c) nitration
- (d) dehydration
- 5. Only carbon is obtained when concentrated H<sub>2</sub>SO<sub>4</sub> is added to:
  - (a) formic acid
- (b) cane sugar
- (c) oxalic acid
- (d) ethyl alcohol
- **6.** Concentrated H<sub>2</sub>SO<sub>4</sub> cannot be used to prepare **HBr** or **HI** from KBr or KI because it:
  - (a) reacts too slowly with KBr or KI
  - (b) reduces HBr or HI
  - (c) oxidises HBr or HI
  - (d) oxidises KBr to KBrO<sub>3</sub> or KI to KIO<sub>3</sub>

### **THOUGHT 2**

The binary compounds of oxygen with other elements are called oxides. They are classified either depending upon their acid-base characteristics or on the basis of oxygen content.

- (a) Normal oxides: These oxides which contain oxygen atoms as permitted by the normal oxidation number, i.e.,
   -2. Normal oxide may be acidic, basic, amphoteric or neutral.
- **(b) Polyoxides:** The oxides which contain oxygen atoms different than those permitted by the normal oxidation number of -2.
  - (i) **Peroxides:** Two oxygen atoms are linked to each other and each oxygen has -1 oxidation number. They contain (O—O)<sup>2-</sup> unit.
  - (ii) Superoxides: These oxides contain  $(O-O)^{-1}$  unit, *i.e.*, each O-atom has oxidation number -1/2.
- (c) Suboxides: These contain low content of oxygen than expected.
- (d) Mixed oxides: These oxides are made of two simpler oxides.
- 1. Which pair of species is referred to as suboxides?
  - (a) CO, NO
- (b) SO<sub>2</sub>, CaO
- (c) N<sub>2</sub>O, CO
- (d)  $N_2O$ ,  $C_3O_2$
- 2. Which of the following pairs contains neutral oxides?
  - (a)  $SO_2$ ,  $SO_3$
- (b)  $N_2O_3, N_2O_5$
- (c) CO, NO
- (d) Na<sub>2</sub>O, CaO
- 3. Which of the following pairs contains mixed oxides?
  - (a)  $Pb_3O_4$ ,  $Fe_3O_4$
- (b) MnO<sub>2</sub>, BaO<sub>2</sub>
- (c)  $KO_2$ ,  $Na_2O_2$
- (d)  $Mn_3O_4$ ,  $N_2O_5$
- 4. Which of the following pairs contains amphoteric oxides ?
  - (a) BeO, BaO
- (b) BeO,  $Al_2O_3$
- (c)  $Al_2O_3$ ,  $P_2O_5$
- (d) FeO, CuO
- 5. Which of the following oxides is paramagnetic in nature?
  - (a) KO<sub>2</sub>

(b) BaO<sub>2</sub>

(c) H<sub>2</sub>O

(d) CO<sub>2</sub>

## THOUGHT 3

Sulphur and rest of the elements of group 16 are less electronegative than oxygen. Therefore, their atoms cannot take up electrons easily. They can acquire  $ns^2np^6$  configuration by sharing two electrons with the atoms of other elements and thus, exhibit +2 oxidation state in their compounds. In addition to this, their

atoms have vacant d-orbitals in their valence shell to which electrons can be promoted from the p and s-orbitals of the same shell. As a result, they can show +4 and +6 oxidation states.

- 1. The oxidation state of sulphur in  $S_8$ ,  $SO_3$  and  $H_2S$  respectively are:
  - (a) 0, +6 and -2
- (b) +2, +6, -2
- (c) 0, +4 and +2
- (d) -2, +6, +2
- 2. The oxidation state of sulphur in Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub> is:
  - (a) 2/3

(b) 3/2

(c) 3/5

- (d) 5/2
- 3. The nature of the compounds of sulphur having +4 oxidation state is:
  - (a) act as oxidising agents
  - (b) act as reducing agents

- (c) act as oxidising as well as reducing agents
- (d) cannot be predicted
- **4.** Like sulphur, oxygen does not show +4 and +6 oxidation states. The reason is:
  - (a) that oxygen is a gas while sulphur is a solid
  - (b) that oxygen has high ionisation enthalpies in comparison to sulphur
  - (c) that oxygen has high electron affinity in comparison to sulphur
  - (d) that oxygen has no d-orbitals in its valence shell.
- 5. Oxygen exhibits +2 oxidation state in:
  - (a) H<sub>2</sub>O

(b) OF<sub>2</sub>

(c) Cl<sub>2</sub>O

(d) H<sub>2</sub>O<sub>2</sub>

Thought 1	1. (d)	2. (a)	3. (d)	<b>4.</b> (c)	<b>5.</b> (b)	<b>6.</b> (c
Thought 2	<b>1.</b> (d)	2. (c)	3. (a)	<b>4.</b> (b)	<b>5.</b> (a)	
Thought 3	1. (a)	2. (d)	3. (c)	<b>4.</b> (d)	5, (b)	

## INTEGER ANSWER Type Questions

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. The number of unpaired electrons in the valence shell of the members of oxygen family is:
- 2. What is oxidation state of sulphur in Caro's acid?
- 3. How many orbitals are involved in the hybridisation of sulphur in SCl<sub>2</sub>?
- 4. How many  $\pi$ -bonds are present in Marshall's acid?
- 5. Ozone reacts with dry iodine to form an oxide having . . . . oxygen atoms in its molecule.
- **6.** How many lone pairs are present in OF<sub>2</sub> molecule?

## Answers

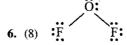
1. (2) Valence shell has six electrons. Out of which two are unpaired.

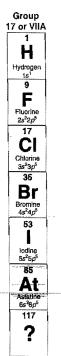
$$\uparrow \downarrow \qquad \uparrow \downarrow \qquad \uparrow \qquad \uparrow$$

2. (6) 
$$H - O - S_{+6} - O - O - H$$

3. (4)  $sp^3$ -hybridisation

- 4. (4) HO S O O S OH  $\parallel 1 \parallel 2 \parallel 1 \parallel 4$   $\downarrow 1 \parallel 2 \parallel 1 \parallel 4$
- 5. (9)  $9O_3 + 2I_2 \longrightarrow I_4O_9 + 9O_2$





# CHAPTER 12

## Elements of Group VIIA or 17

(Halogens)

### Contents:

- 12.1 Position in Periodic Table
- 12.2 Anomalous Behaviour of Fluorine
- 12.3 Fluorine
- 12.4 Chlorine
- 12.5 Bromine
- **12.6** Iodine
- 12.7 Halogen Acids or Hydracids
- 12.8 Oxides of Chlorine
- 12.9 Oxy-Acids of Chlorine
- 12.10 Interhalogen Compounds
- 12.11 Polyhalides
- 12.12 Basic Properties of Iodine
- 12.13 Pseudohalides and Pseudohalogens

### 12.1 POSITION IN PERIODIC TABLE

17th or VIIA group of the periodic table (extended form) consists of five elements; fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). This group of five elements forms a family known as halogen family as their salts are found in sea water. Halogen is a Greek word meaning a sea salt. Halogens are p-block elements as the last differentiating electron is accommodated on np subshell. These elements have seven electrons in their valency shell and thus placed in VII group of the periodic table.

Group Period	VIA 16	- VIIA 17	Zero 18
-		H*	He
. 1		(1)	(2)
_	0	F	Ne
2	(8)	(9)	(10)
	S	Cl	Ar
3	(16)	(17)	(18)
	Se	Br	Kr
4	(34)	(35)	(36)
_	Te	· I	Xe
5	(52)	(53)	(54)
_	Po	At	Rn
6	(84)	(85)	(86)
_	Uuh		Uuo
7	(116)	?	(118)

Except astatine, the members are found in combined state in considerable quantities in nature. Astatine is unstable element of radioactive origin. Astatine is radioactive artificially prepared element. These elements possess same electronic configuration and show similarities as well as gradual gradation in their physical and chemical properties. Thus, the inclusion of these elements in the same subgroup is justified. However, like other groups, the first element fluorine differs from other elements of the group in some respects.

### 1. Electronic Configuration

The electronic configurations of halogens are given as:

Element	At. No.		Electronic configuration	With inert gas core
Fluorine	9	2, 7	$1s^2$ , $2s^2 2p^5$	[He] $2s^22p^5$
Chlorine	17	2, 8, 7	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^5$	[Ne] $3s^23p^5$
Bromine	35	2, 8, 18, 7	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^5$	[Ar] $3d^{10}$ , $4s^24p^5$
Iodine	53	2, 8, 18, 18, 7	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}$ , $5s^2$ $5p^5$	[Kr] $4d^{10}$ , $5s^25p^5$
Astatine	85	2, 8, 18, 32, 18, 7	$1s^2$ , $2s^2$ $2p^6$ , $3s^2$ $3p^6$ $3d^{10}$ , $4s^2$ $4p^6$ $4d^{10}4f^{14}$ , $5s^2$ $5p^6$ $5d^{10}$ , $6s^2$ $6p^5$	[Xe] $4f^{14}$ , $5d^{10}$ , $6s^26p^5$

Note: The last member of group 17 or VIIA with atomic number 117 (ununseptium) is yet to be discovered.

<sup>\*</sup>Sometimes hydrogen, the lightest element, is also included in group VIIA or 17.

All the halogens have seven electrons  $(ns^2np^5)$  in their outermost shell. The electrons in np-orbitals are distributed as  $np_x^2$ ,  $np_y^2$ ,  $np_z^1$ . The penultimate shell in F has 2 electrons, in Cl 8 electrons and in Br, I and At 18 electrons. This shows why fluorine differs from chlorine and these two differ from the remaining elements.

Since the halogens have only one electron less than the number present in the adjacent noble gas, they have a tendency to take up one electron to acquire the stable noble gas configuration. Hence, the halogens are very reactive elements.

### 2. Physical Characteristics

(a) Physical state: The tendency to form condensed molecules increases with increase in atomic number. Fluorine and chlorine are gases at ordinary temperature, bromine is a highly fuming liquid while iodine is a volatile solid.

F	Cl	Br	I
Gas	Gas	Fuming liquid	Volatile solid

Halogens exist as diatomic covalent molecules. These molecules are held together by weak van der Waals' forces. On account of weak intermolecular forces, the halogens are volatile in nature. With the increase in size, these forces increase from fluorine to iodine and hence change in physical state occurs from gas  $(F_2 \text{ and } Cl_2)$  to solid  $(I_2)$ .

(b) Atomic and ionic radii: The halogens have the lowest values of atomic radii in their respective periods. This is due to maximum effective nuclear charge of the halogen in its respective period. However, the atomic radii and ionic radii  $(X^-)$  ion) increase gradually from fluorine to iodine.

Element	F	Cl	Br	I
Atomic radii (pm)	64	99	114	133
Ionic radii (pm) (X <sup>-</sup> )	133	184	196	220
	Increase gradually			

As we move from fluorine to astatine, an extra shell of electrons is added to each element. The addition of an extra shell increases the atomic and ionic radii from fluorine to astatine. The radius of the halide ion is always greater than the corresponding halogen atom.

(c) Atomic volume and density: These increase steadily from fluorine to iodine.

Element	F	CI	Br	I	
At. volume (mL)	17.1	18.7	23.5	25.7	
Density (in liquid state)	1.5	1.66	3.19	4.94 (solid)	
$(g cm^{-3})$	at 85 K	at 203 K	at 273 K	at 293 K	
	Increase gradually				

(d) Energy and stability of X—X bond: With the increase of size, the bond length increases from fluorine to iodine. Since the bond length of fluorine is minimum, its bond dissociation energy should be highest. However, the bond dissociation energy of fluorine is less than Cl—Cl and Br—Br.

Actually, the bond dissociation energy should have decreased from fluorine to iodine but it starts decreasing from chlorine to iodine.

X— $X$ bond	FF	Cl—Cl	BrBr	I—I
Bond length (pm)	142	199	228	267
Bond dissociation	158.8	242.6	192.8	151.1
energy (kJ/mol)				

It has been suggested by Coulson that the lower value of bond dissociation energy of fluorine is due to the high interelectronic repulsions between non-bonding electrons in the 2p-orbitals of fluorine. As a result, F—F bond is weaker in comparison to Cl—Cl and Br—Br bonds. Thus, the bond dissociation energy follows the sequence:

$$Cl_2 > Br_2 > F_2 > I_2$$

(e) Ionisation enthalpy: The ionisation enthalpies of halogens are very high. This indicates that the halogens have a little tendency to lose electron to form  $X^+$  cation. However, the ionisation enthalpies decrease from F to I, *i.e.*, the tendency to form cation increases from F to I as the size of halogen increases.

Element	F	Cl	Br	I
First ionisation	1680	1256	1142	1008
enthalpy (kJ mol <sup>-1</sup> )		Decreases	gradually	·.

Iodine having the lowest value of ionisation potential has some tendency to form I<sup>+</sup> ion as it forms compounds like ICl, ICN, etc., which in molten state conduct electricity showing the existence of I<sup>+</sup> cation.

**(f) Electron affinity:** Electron affinity values are high in the case of halogens as they have one electron less than the nearest noble gas configuration, and have a strong tendency to accept an additional electron.

The low value of electron affinity of fluorine is probably due to small size of fluorine atom, *i.e.*, electron density is high which hinders the addition of an extra electron. As we move down from chlorine onwards, the electron affinity values become less and less negative as the size of the halogen increases. Thus, electron affinity follows the sequence:

Cl (-349 kJ 
$$\text{mol}^{-1}$$
) > F (-333 kJ  $\text{mol}^{-1}$ ) > Br (-325 kJ  $\text{mol}^{-1}$ ) > I (-296 kJ  $\text{mol}^{-1}$ )

(g) Electronegativity: The halogens have high values of electronegativities. Fluorine has the maximum electronegativity. The electronegativity decreases from fluorine to iodine.

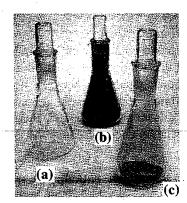
As a result of the decrease of electronegativity, the non-metallic character decreases from fluorine to iodine. Metallic

character is observed in iodine as it forms in a few cases a positive ion and has a metallic lustre.

**(h) Colour:** All the halogens are coloured. The colour deepens with the rise of atomic number from fluorine to iodine.

The colour is due to the absorption of energy from visible light by their molecules for excitation of outer electrons to higher energy levels. Fluorine absorbs violet portion of the light and thus appears yellow while iodine absorbs yellow and green portions of the light and thus appears violet.

Change in colour on moving down this group is called blue shift or bathochromic shift.



Colour of Halogens

- (a) Colour of Chlorine (Cl<sub>2</sub>)—Yellow green
- (b) Colour of Bromine (Br<sub>2</sub>)—Reddish brown
- (c) Iodine (I2)-Deep violet

Fig. 12.1

(i) Oxidation states: Since these elements have seven electrons in their valency shell, each element tries to attain 8 electrons either by accepting an electron from an element which is less electronegative than it or by sharing its unpaired electron in p-orbital with another element. When the halogen atom combines with an element of lesser electronegativity, it shows -1 oxidation state. On the other hand, when it combines with an element having higher electronegativity, it exhibits +1 oxidation state. Fluorine, being the most electronegative, always shows -1 oxidation state only.

Chlorine, bromine and iodine show positive oxidation states as the electrons in the valency shell can be promoted to vacant d-orbitals. These elements (*i.e.*, Cl, Br and I) can show +3, +5 and +7 oxidation states depending on the number of singly occupied orbitals, *i.e.*, oxidation states lie between -1 to +7.

Halogen atom  $\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow$ (except F atom) in the ground state. 1 unpaired electron; -1 or +1  $(ns^2np^5)$ oxidation state Halogen atom in the first excited state.  $(ns^2np^4nd^1)$ 3 unpaired electrons; +3 oxidation state Halogen atom in the  $|\uparrow\downarrow\downarrow|$   $|\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$ second excited state.  $(ns^2np^3nd^2)$ 5 unpaired electrons; +5 oxidation state ndHalogen atom in the  $|\uparrow|\uparrow|\uparrow|\uparrow|\uparrow|\uparrow|\uparrow|\uparrow$ third excited state.  $(ns^1np^3nd^3)$ 7 unpaired electrons; +7 oxidation state F atom has no d-orbitals in the valency shell, thus it cannot have any excited state and consequently cannot show any of the higher oxidation states. In the case of bromine, the penultimate shell (i.e.,  $3s^23p^63d^{10}$ ) is weakly screening and hence the energy required to promote an electron from 4s-orbital is higher than in chlorine and thus bromine does not show +7 oxidation state.

Besides +3, +5 and +7 oxidation states, +4 and +6 oxidation states are also shown by these elements in oxides and oxyacids.

### **Examples:**

Oxidation state	Fluorine	Chlorine.	Bromine	Iodine
-1	NaF, OF <sub>2</sub> ,	NaCl, MgCl <sub>2</sub> ,	NaBr, CaBr <sub>2</sub> ,	NaI, AgI,
	ClF <sub>3</sub> ,IF <sub>5</sub>	AgCl, HCl	AgBr, HBr	HI, CaI <sub>2</sub>
+1	×	HClO, Cl <sub>2</sub> O	HBrO, Br <sub>2</sub> O	HIO, ICl
+3	×	CIF <sub>3</sub> , HClO <sub>2</sub>	BrF <sub>3</sub>	ICl <sub>3</sub>
+4	×	ClO <sub>2</sub>	BrO <sub>2</sub>	$I_2O_4$
+5	- x	HClO <sub>3</sub>	HBrO <sub>3</sub> , BrF <sub>5</sub>	HIO <sub>3</sub> , IF <sub>5</sub>
+6	×	Cl <sub>2</sub> O <sub>6</sub>	BrO <sub>3</sub>	×
+7	×	HClO <sub>4</sub>	×	HIO <sub>4</sub> , IF <sub>7</sub>

(j) Reduction potentials and oxidising nature: Standard reduction potentials of halogens are positive and decrease from fluorine to iodine. Thus, halogens act as strong oxidising agents and their oxidising power decreases from fluorine to iodine.

Element F Cl Br I

Reduction potential

(
$$E^{\circ}$$
 volt) +2.87 +1.36 +1.09 +0.54

Decreases gradually

Oxidising nature also decreases

The strength of an oxidising agent depends on several energy terms as shown below:

$$\frac{1}{2}X_{2}(\text{solid}) \xrightarrow{\frac{1}{2}\text{heat of}} \frac{1}{2}X_{2}(\text{liq.}) \xrightarrow{\frac{1}{2}\text{heat of}} \underbrace{\frac{1}{2}X_{2}(\text{gas})} \xrightarrow{\frac{1}{2}\text{heat of}} X(\text{gas})$$

$$\downarrow \text{Oxid.} \quad \text{Electron} \quad \text{potential} \quad \text{Effinity} \downarrow$$

$$X^{-}(\text{hyd.}) \xleftarrow{\text{Heat of}} X^{-}(\text{gas})$$

$$E = \frac{1}{2}H_f + \frac{1}{2}H_{ev} + \frac{1}{2}H_d$$
 - electron affinity -  $H_{hyd}$ .

The E values decreases from fluorine to iodine.

Fluorine is the strongest oxidising agent. It will oxidise other halide ions to halogens in solution or when dry.

F<sub>2</sub> + 2
$$X^ \longrightarrow$$
 2F<sup>-</sup> +  $X_2$   
( $X^-$  = Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>)

Similarly, chlorine will oxidise  $Br^-$  and  $I^-$  solution to  $Br_2$  and  $I_2$ , respectively and  $Br_2$  will oxidise  $I^-$  to  $I_2$ . In general, a

halogen of low atomic number will oxidise the halide ion of higher atomic number.

The halide ions act as reducing agents. F ion does not show any reducing nature but Cl, Br and I ion act as reducing agents and their reducing nature is in increasing order.

$$\xrightarrow{\text{CI}^-} \xrightarrow{\text{Br}^-} \xrightarrow{\text{I}^-}$$
Reducing nature increases

**(k) Solubility:** Halogens, being non-polar molecules, do not dissolve to a considerable extent in a polar solvent like water. However, fluorine reacts with water readily forming a mixture of oxygen and ozone.

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$
  
 $3F_2 + 3H_2O \longrightarrow 6HF + O_3$ 

C1<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub> are more soluble in organic solvents such as CCl<sub>4</sub>, CHCl<sub>3</sub>, paraffins and produce coloured solutions. Chlorine, bromine and iodine give yellow, brown and violet colour, respectively, in chloroform or carbon tetrachloride. It is believed that in non-polar solvents halogens exist as free molecules.

In nucleophilic solvents like alcohols, ketones, liquid sulphur dioxide, halogens produce brown solutions. It is due to complex formation (solvent  $\rightarrow$  halogen).

### 3. Chemical Characteristics

(a) **Reactivity:** Halogens are most reactive non-metallic elements, high reactivity is due to low dissociation energies of the halogen molecules and high electron affinities.

Molecule 
$$N_2$$
  $O_2$   $H_2$   $X_2$  (halogen) Dissociation energy 225 118.3 103.2 35.5 to 57.2 (kcal/mol)

In halogens, fluorine is most reactive and iodine is least reactive.

This is due to following factors:

- (i) As the size increases, the attraction for an additional electron by the nucleus becomes less. Thus, reactivity decreases.
- (ii) Due to decrease in electronegativity from F to I, the bond between halogen and other elements becomes weaker and weaker. Fluorides are most stable while iodides are least.
  - (iii) Dissociation energies of X—X bonds are low.

The following reactions illustrate the relative reactivity of halogens.

(i) Reaction towards water: Fluorine decomposes water very readily even at low temperature and in dark forming mixture of O<sub>2</sub> and O<sub>3</sub>, Cl<sub>2</sub> decomposes water in presence of sunlight while bromine decomposes water very slowly in presence of sunlight. Iodine does not decompose water.

$$\begin{array}{c} X_2 + \text{H}_2\text{O} & \xrightarrow{\text{Sunlight}} & \text{H}X + \text{H}X\text{O} \\ \text{(C1}_2 \text{ or } \text{Br}_2\text{)} & & \text{3F}_2 + 3\text{H}_2\text{O} & \longrightarrow & \text{6HF} + \text{O}_3 \\ 2\text{F}_2 + 2\text{H}_2\text{O} & \longrightarrow & \text{4HF} + \text{O}_2 \\ \text{I}_2 + \text{H}_2\text{O} & \longrightarrow & \text{No reaction} \end{array}$$

(ii) Reaction with metals and non-metals: Nearly all metals combine with fluorine either in cold or on heating forming fluorides. Chlorine combines with large number of metals but

slowly. Bromine and iodine do not react with noble metals like Au, Pt and even with less active metals.

Halogens also combine with a number of non-metals like S, P, As, etc. The reactivity decreases from fluorine to chlorine. For example, sulphur forms hexafluoride with fluorine (SF<sub>6</sub>), tetrachloride with chlorine (SCl<sub>4</sub>) and dibromide with bromine (SBr<sub>2</sub>) and there is no reaction between sulphur and iodine.

(iii) Reaction with hydrocarbons: Fluorine brings decomposition of the hydrocarbon and also forms fluorinated products readily.

$$CH_4 + 2F_2 \longrightarrow C + 4HF$$

Chlorine and bromine give substitution reactions. The rates of reactions with bromine are slow. Iodine has practically no action on hydrocarbons.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

**(b) Hydrides of the halogens (Hydrogen halides):** All the halogens react with hydrogen to form volatile covalent hydrides of formula HX. These hydrides are called hydracids. The activity of halogens towards hydrogen decreases from fluorine to iodine.

Hydrogen combines explosively with fluorine even in dark. It combines with chlorine in presence of sunlight and with bromine on heating. Hydrogen combines with iodine on heating and in presence of a catalyst. The reaction with iodine is reversible and incomplete. Detailed discussion is given in section 12.7.

(c) Oxides: The compounds of oxygen and fluorine are not called as oxides but oxygen fluorides as fluorine is more electronegative than oxygen. The compounds of oxygen and rest of the halogens are termed oxides. Halogens and oxygen do not combine directly with each other. However, these compounds have been obtained indirectly. The known compounds are:

$$\begin{array}{cccc} OF_2 & Cl_2O & Br_2O & I_2O \\ O_2F_2 & ClO_2 & BrO_2 \\ & Cl_2O_6 & BrO_3 \\ & Cl_2O_7 & \end{array}$$

In these oxides, bonds are mainly covalent due to small difference in the electronegativity of oxygen and the halogens. Oxygen fluorides do not form oxyacids. Oxides of chlorine are acidic and the acidic nature increases as % of oxygen increases. Thus, Cl<sub>2</sub>O is least acidic while Cl<sub>2</sub>O<sub>7</sub> is most acidic oxide.

$$Cl_2O + H_2O \Longrightarrow 2HClO$$
  
 $2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$   
 $Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$   
 $Cl_2O_7 + H_2O \longrightarrow 2HClO_4$ 

The oxides of bromine and iodine are also acidic in nature. All the three monoxides, viz., OF<sub>2</sub>, Cl<sub>2</sub>O and Br<sub>2</sub>O have tetrahedral structure involving  $sp^3$  hybridization of oxygen; bond angle increases with increase in size of halogen atom.

(d) Oxyacids:	Fluorine does not form any oxyacid as it is more electronegative than oxygen. Other halogens form oxyacids
of the type $HXO$ , I	HXO <sub>2</sub> , HXO <sub>3</sub> and HXO <sub>4</sub> . Some of the acids are quite unstable and are known only in solutions or as their
salts. List of oxyac	eids is given below:

Oxidation number	Oxyacids of					a		
of halogen	Cl	Br	,I	General name	Acidity	Stability	Oxidising nature	
+1	HClO	HBrO	HIO	Hypo-halous	. 1		1.0	
+3	HClO <sub>2</sub>			Halous	ases	ases	creases	
+5	HClO <sub>3</sub>	HBrO <sub>3</sub>	HIO <sub>3</sub>	Halic	Incre	Incre	Decr	
+7	HClO <sub>4</sub>		HIO <sub>4</sub> (H <sub>5</sub> IO <sub>6</sub> )	Perhalic		1	1	

Acidity decreases ----

Note: Greater is the oxidation state of central halogen atom more will be the acidic character.

### General properties

- (i) In oxyacids, the hydrogen is a part of an —OH group and not directly attached to the halogen atom. The oxyacids are monobasic and form one series of salts.
- (ii) In oxyacids of the same halogen in different oxidation states, the acidic nature and thermal stability increase while oxidising nature decreases with the increase of oxidation state of the halogen. For example, for the four oxyacids of chlorine, the acidic character and thermal stability are in the order:

while the oxidising power is in the order:

$$HCIO > HCIO_2 > HCIO_3 > HCIO_4$$

- i.e., increasing oxygen content leads to:
- (a) an increase in thermal stability
- (b) an increase in strength of the acid
- (c) a decrease in oxidising power.
- (iii) In the oxyacids of different halogens in the same oxidation state, the thermal stability and acidic nature, in general, decrease with increase of atomic number. However, in HXO<sub>3</sub>, HIO<sub>3</sub> is most stable.
- **(e) Reaction with alkalies:** Fluorine reacts with cold dilute alkalies yielding OF<sub>2</sub> (oxygen difluoride) and with conc. alkalies evolve oxygen.

$$\begin{array}{ccc} 2NaOH + 2F_2 & \longrightarrow & 2NaF + OF_2 + H_2O \\ \text{(Cold and dilute)} \end{array}$$

$$4NaOH + 2F_2 \longrightarrow 4NaF + O_2 + 2H_2O$$

Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub> behave similarly but differently than fluorine, with cold dilute alkalies, they form a mixture of halide and hypohalite and with concentrated hot alkalies a mixture of halide and halate.

2NaOH + Cl<sub>2</sub> 
$$\longrightarrow$$
 NaCl + NaClO + H<sub>2</sub>O Sodium Sodium chloride hypochlorite

$$\begin{array}{cccc} 6\text{NaOH} + 3X_2 & \longrightarrow & 5\text{Na}X + \text{Na}X\text{O}_3 + 3\text{H}_2\text{O} \\ \text{Hot and conc.} & \text{Halide} & \text{Halate} \\ \hline & 6\text{NaOH} + 3I_2 & \longrightarrow & 5\text{NaI} + \text{NaIO}_3 + 3\text{H}_2\text{O} \\ \hline & & \text{Sod. iodide Sod. iodate} \\ \end{array}$$

(f) Interhalogen compounds: The halogens on account of difference in their electronegativities combine with each other to form compounds of type  $AB_n$  where A is always bigger atom and B is smaller atom and 'n' may have values 1, 3, 5 and 7. These are covalent compounds and called interhalogen compounds. The value of 'n' increases with the increase of size of halogen A. Maximum value of 'n' for chlorine is 3, for bromine 5 and for iodine 7. The known interhalogen compounds are listed below:

AB type : CIF, BrF, BrCl, ICl, IBr  $AB_3$  type : CIF<sub>3</sub>, BrF<sub>3</sub>, ICl<sub>3</sub>  $AB_5$  type : IF<sub>5</sub>, BrF<sub>5</sub>  $AB_7$  type : IF<sub>7</sub>

The interhalogen compounds are gases or liquids. These are volatile and fume in air. In general, these compounds are more reactive than pure halogens except fluorine because A—B bond is weaker than B—B bond. These are hydrolysed and act as oxidising agents. The compounds of iodine and fluorine are thermally more stable while the compounds of iodine and chlorine or iodine and bromine are less stable.

# 12:2\* ANOMALOUS BEHAVIOUR OF FLUORINE

Fluorine differs from other members of its own sub-group due to the following reasons:

- (i) Small size of the atom in comparison to the sizes of Cl, Br and I atoms.
  - (ii) Highest electronegativity.
  - (iii) Absence of *d*-orbitals in its valency shell.
  - (iv) Highest positive reduction potential.

The main points of difference are:

(1) Fluorine shows only a negative oxidation state of -l due to maximum value of electronegativity. It never shows any

positive oxidation state. The other halogens show negative as well as positive oxidation states, *i.e.*, between -1 and +7.

- (2) Fluorine is most reactive as bond dissociation energy of F—F bond is low. X—X bond is stronger in Cl<sub>2</sub> and Br<sub>2</sub>.
- (3) Maximum covalency of fluorine is one as there is no d-orbital in its valency shell. Other members can have maximum covalency of 7 because of vacant d-orbitals.
- (4) HF is a weak acid in comparison to HCl, HBr and HI under similar circumstances. HF is a liquid (b.pt. 19°C) while HCl, HBr and HI are gases under ordinary conditions. This is due to presence of hydrogen bonding in HF while hydrogen bonding is not present in HCl, HBr and HI.
- (5) Hydrofluoric acid is a dibasic acid  $(H_2F_2)$  while HCl, HBr and HI are monobasic in nature. Thus, hydrofluoric acid forms two series of salts such as NaHF<sub>2</sub>, Na<sub>2</sub>F<sub>2</sub>. Most of the fluorides are ionic. These contain  $F^-$  ion while other halides have frequently molecular lattices.
- (6) AgF is soluble in water while AgCl, AgBr and AgI are insoluble in water. Similarly, calcium fluoride is insoluble and other halides of calcium are soluble.
- (7) Fluorine combines with sulphur to form SF<sub>6</sub> but no other halogen forms the hexahalide with sulphur.
- (8) Fluorine does not form any oxyacid but other halogens form a number of oxyacids.
- (9) It directly combines with carbon while other halogens do not react even under drastic conditions.
- (10) Ozone is formed when fluorine decomposes water. Ozone is not formed when other halogens react with water.
- (11) Fluorine does not form any oxysalt when it reacts with alkalies while other halogens form oxysalts with alkalies.
- (12) Fluorides are more stable than corresponding chlorine compounds. For example, UF<sub>6</sub> is more stable than UCl<sub>6</sub>. NF<sub>3</sub> is non-explosive while NCl<sub>3</sub> is highly explosive.
- (13) The fluoride ion has a great tendency to form complex ions, e.g.,  $[AIF_6]^{3-}$ ,  $[FeF_6]^{3-}$ . The remaining halide ions show this tendency to a much lesser extent.
- (14) Fluorine does not have vacant d-orbital in valence shell therefore it does not combine with F ion to form polyfluoride ions like  $Cl_3^-$ ,  $Br_3^-$ ,  $I_3^-$ ,  $I_5^-$ , etc.

### Similarities between oxygen and fluorine:

- 1. Atomic and ionic radii of both elements are very similar.
- 2. Both exist in gaseous state at room temperature.
- 3. Hydrides of both elements form associated species due to hydrogen bond formation.

$$(HF)_x$$
,  $(H_2O)_x$ 

- 4. Hydrides of both elements have abnormally high b.pts.
- 5. Hydrides of both elements are ionizing solvents.

## 12.3 FLUORINE

**Occurrence:** Fluorine is extremely reactive and hence does not occur in free state. It is widely found in the combined state as fluorides. The important minerals are:

(i) Fluorspar (Fluorite) , CaF<sub>2</sub>

(ii) Cryolite , Na<sub>3</sub>AlF<sub>6</sub>

(iii) Fluorapatite ,  $CaF_2 \cdot 3Ca_3(PO_4)_2$ 

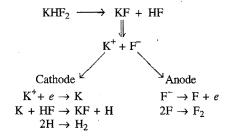
It is present in small amount as fluorides in plant-ashes, soil, sea water, bones and teeth of animals. It constitutes nearly 0.054% of earth's crust.

**Isolation:** Fluorine presented many difficulties in its isolation. It remained a difficult problem in chemistry for many years and after a hard labour of many chemists for about 75 years it could be isolated finally by **Moissan** in 1886. **The reasons for its late discovery were its high reactivity and non-conducting nature of hydrofluoric acid.** Fluorine attacked the material of the vessels used for its isolation. Carbon vessel was attacked with formation of CF<sub>4</sub> and platinum vessel was reduced to chocolate powder. The vessels of other metals were also affected. The platinum and carbon could not be used as electrodes. Another difficulty experienced was that when the electrolysis of aqueous hydrofluoric acid was carried out, hydrogen and oxygen (ozone) were obtained and when anhydrous hydrofluoric acid was tried it was found to be a bad conductor of electricity.

Moissan finally solved the problem and isolated fluorine by the electrolysis of anhydrous hydrofluoric acid in the presence of potassium hydrogen fluoride using Pt–Ir alloy vessel at -23°C. The electrodes used were also of Pt–Ir alloy.

**Modern methods of isolation:** In modern methods, fluorine is prepared by electrolysis of a fused fluoride (usually potassium hydrogen fluoride, KHF<sub>2</sub>). The electrolytic cells are made of copper, nickel or monel metal. The anode is generally of graphite and the fluorine set free contains some carbon tetrafluoride.

### Reactions in the electrolytic cell



The precautions given ahead should be taken in the preparation of fluorine:

- (i) The electrolyte must be completely dry. In presence of moisture, the evolved fluorine reacts with moisture to form  $\rm O_2$  and  $\rm O_3$ .
- (ii) The parts of the apparatus which come in contact with fluorine must be free from oil and greese.
- (iii) The vessel in which fluorine is collected should also be absolutely dry.
- (iv) The gas must be made free from HF before storing by passing through sodium fluoride (NaF) otherwise HF will attack vessel.

[Note: HF is more corrosive and reactive than fluorine.]

The electrolytic cells used are:

(a) Dennis cells and (b) Whytlaw-Gray cell

### Properties

(a) The gas is pale greenish yellow in colour. It can be condensed to yellow liquid at -188°C and pale yellow solid at -223°C. (b) It has pungent odour resembling that of a mixture of ozone and chlorine. (c) It is a poisonous gas but less poisonous than HF gas. (d) It is the most reactive element.

(i) It can displace all the halogens from their halides.

$$F_2 + 2NaX \longrightarrow 2NaF + X_2$$
  
 $(X = Cl^-, Br^- \text{ or } I^-)$   $(X_2 = Cl_2, Br_2 \text{ or } I_2)$ 

(ii) It combines with most of the metals and non-metals to form fluorides.

$$2Ag + F_2 \longrightarrow 2AgF$$

$$2Al + 3F_2 \longrightarrow 2AlF_3$$

$$Mg + F_2 \longrightarrow MgF_2$$

Hydrogen explodes violently in fluorine even in the dark.

$$H_2+F_2 \longrightarrow H_2F_2$$

A mixture of oxygen and fluorine explodes in presence of silent electric discharge.

$$O_2 + F_2 \longrightarrow O_2F_2$$
 (Dioxygen difluoride)

It reacts with wood charcoal, phosphorus, arsenic, antimony, boron, silicon producing a flame.

$$C+2F_2 \longrightarrow CF_4$$
;  $Si + 2F_2 \longrightarrow SiF_4$   
 $2P + 3F_2 \longrightarrow 2PF_3$ ;  $2As + 3F_2 \longrightarrow 2AsF_3$   
 $2B + 3F_2 \longrightarrow 2BF_3$ 

However, fluorine does not react with oxygen, nitrogen and inert gases directly under ordinary conditions.

(iii) Fluorine reacts vigorously with water giving  $O_2$  and  $O_3$ .

$$2H_2O + 2F_2 \longrightarrow 4HF + O_2$$
  
 $3H_2O + 3F_2 \longrightarrow 6HF + O_3$ 

(iv) Fluorine reacts with dilute alkalies to form oxygen difluoride (OF<sub>2</sub>) and with conc. alkalies O<sub>2</sub> is formed.

$$2F_2 + 2NaOH \longrightarrow OF_2 + 2NaF + H_2O$$
  
 $2F_2 + 4NaOH \longrightarrow 4NaF + 2H_2O + O_2$ 

(v) It acts as a strong oxidising agent. It oxidises chlorates to perchlorates, iodates to periodates and bisulphates to peroxysulphates.

$$KClO_3 + F_2 + H_2O \longrightarrow KClO_4 + H_2F_2$$
  
 $KlO_3 + F_2 + H_2O \longrightarrow KlO_4 + H_2F_2$   
 $2NaHSO_4 + F_2 \longrightarrow Na_2S_2O_8 + 2HF_2$ 

- (vi) It attacks glass at about 100°C forming SiF<sub>4</sub>. However, the attack of dry fluorine is slow. At low temperatures, dry fluorine can be stored in dry glass vessel.
- (vii) It reacts with hydrocarbons explosively and forms fluorinated hydrocarbons.

$$CH_4 \xrightarrow{F_2} CH_3F$$
  $F_2$   $CH_2F_2$   $F_2$   $CHF_3$   $F_2$   $CF_4$ 

Fluorine reacts with NH<sub>3</sub> to form nitrogen and H<sub>2</sub>S forming SF<sub>6</sub> (H<sub>2</sub>S burns).

$$2NH_3 + 3F_2 \longrightarrow N_2 + 6HF$$
  
 $H_2S + 4F_2 \longrightarrow SF_6 + 2HF$ 

- (viii) It combines with xenon to form XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub> (See inert gases).
  - (ix) Fluorination of methanol.

$$CH_3OH + 4F_2 \xrightarrow{AgF_2} CF_3OF + 4HF$$

CF<sub>3</sub>OF is very strong oxidising agent.

### **Uses**

- 1. It is used as an insecticide.
- 2. It is extensively used for the preparation of various fluorine compounds which have wide applications.
- (a) Freon, CCl<sub>2</sub>F<sub>2</sub> (dichloro difluoro methane), is used in refrigerators and cold storage plants.
- (b) Teflon  $(C_2F_4)_x$ , a new plastic, has a very high electrical resistance and is used as insulating material in cables. Teflon is not affected by acids, alkalies and strong oxidising agents.
- (c) H<sub>2</sub>F<sub>2</sub> is used for etching of glass and for removing silica from iron castings.

$$SiO_2 + 2H_2F_2 \longrightarrow SiF_4 + 2H_2O$$

- (d)  $UF_6$  is used in the separation of  $U^{235}$  from natural uranium by diffusion method.
- (e) SF<sub>6</sub> has insulating properties. It is used in X-ray and high voltage machines.
  - (f) Sodium fluoroacetate is used as a rat poison.
  - (g) NaF and Na<sub>3</sub>AlF<sub>6</sub> (cryolite) are used as insecticides.
- (h) CuF<sub>2</sub> is used in the ceramic industry and as a flux in soldering, welding and glazing.

### 12.4 CHLORINE

Chlorine was discovered by **Scheele** in 1774 by the action of HCl on MnO<sub>2</sub>. **Berthollet** named this gas oxymuriatic acid gas since he thought it to be an oxide of muratic acid (old name of HCl). In 1810, **Davy** established its elementary nature and named it chlorine on account of its greenish yellow colour (Greek, *chloros* = greenish yellow).

**Occurrence:** Chlorine is widely distributed in nature in the combined state in the form of chlorides of various metals. Common salt (NaCl) is the most important chloride which occurs in sea water, lakes and in rocks. The other important chloride minerals are:

- (i) Sylvite (potassium chloride), KCl
- (ii) Carnallite, KCl, MgCl<sub>2</sub>·6H<sub>2</sub>O
- (iii) Chlorapatite, 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·CaCl<sub>2</sub>
- (iv) Horn silver, AgCl

**Preparation:** (i) By the oxidation of hydrochloric acid. The oxidising agents which can be used are MnO<sub>2</sub>, PbO<sub>2</sub>, Pb<sub>3</sub>O<sub>4</sub> (red lead), KMnO<sub>4</sub> (Potassium permanganate), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Potassium dichromate), NaClO (Sodium hypochlorite), O<sub>3</sub>, etc.

(a) 
$$MnO_2 + 2HCl \longrightarrow MnCl_2 + H_2O + O$$
  
 $2HCl + O \longrightarrow H_2O + Cl_2$   
 $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$   
(b)  $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$   
(c)  $Pb_3O_4 + 6HCl \longrightarrow 3PbCl_2 + 3H_2O + O$ 

(d) 
$$2KMnO_4 + 6HCl \longrightarrow 2KCl + 2MnCl_2 + 3H_2O + 5[O]$$
  
 $10HCl + 5O \longrightarrow 5H_2O + 5Cl_2$ 

$$2KMn\Theta_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

(e) 
$$K_2Cr_2O_7 + 8HCl \longrightarrow 2KCl + 2CrCl_3 + 4H_2O + 3[O]$$
  
6HCl + 3O  $\longrightarrow 3H_2O + 3Cl_2$ 

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

(f) NaClO 
$$\longrightarrow$$
 NaCl + O  
2HCl + O  $\longrightarrow$  H<sub>2</sub>O + Cl<sub>2</sub>  
NaClO + 2HCl  $\longrightarrow$  NaCl + H<sub>2</sub>O + Cl<sub>2</sub>

(g) 
$$\cdot O_3 + 2HCl \xrightarrow{\sim} O_2 + H_2O + Cl_2$$

(ii) By the action of mineral acids or carbon dioxide on bleaching powder.

$$CaOCl2 + H2SO4 \longrightarrow CaSO4 + H2O + Cl2$$

$$CaOCl2 + 2HCl \longrightarrow CaCl2 + H2O + Cl2$$

$$CaOCl2 + CO2 \longrightarrow CaCO3 + Cl2$$

(iii) By heating any chloride with concentrated H<sub>2</sub>SO<sub>4</sub> in presence of MnO<sub>2</sub>.

$$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + O$$
  
 $[NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl] \times 2$   
 $2HCl + O \longrightarrow H_2O + Cl_2$ 

 $2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$ 

**Laboratory preparation:** The following methods are used in the laboratory for the preparation of chlorine:

### (i) By the Action of HCl on MnO<sub>2</sub>

The common method of preparing chlorine in the laboratory is by heating concentrated hydrochloric acid with manganese dioxide in a round-bottom flask fitted with a thistle funnel and a delivery tube (Fig. 12.3).

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

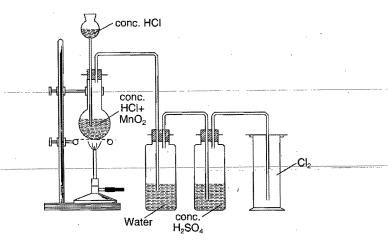


Fig 12.3

Small quantity of  $MnO_2$  is taken in the flask. Concentrated HCl is so adjusted that the end of the thistle funnel remains dipped in it. The contents are heated slowly. The yellowish green gas is evolved. The gas is usually contaminated with water vapours and HCl gas. The evolved gas is first passed through water (to remove HCl gas) and then through conc.  $H_2SO_4$  (to remove water vapours). The chlorine is finally collected in a jar by upward displacement of air.

### (ii) By the Action of HCI on KMnO<sub>4</sub>

This is a convenient method to prepare chlorine in the laboratory. It consists the addition of cold concentrated HCl on potassium permanganate crystals.

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 3Cl_2$$
  
The apparatus used is shown in Fig. 12.4.

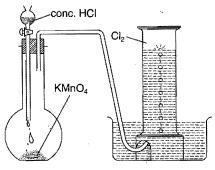


Fig. 12.4

A small quantity of potassium permanganate is placed in the flat-bottom flask fitted with a dropping funnel and a delivery tube. HCl is added drop by drop from the dropping funnel. A

brisk reaction occurs and yellowish-green gas is evolved. It is passed through water and conc. H<sub>2</sub>SO<sub>4</sub> and finally, dry and pure chlorine is collected in a jar by upward displacement.

**Pure chlorine:** It may be obtained by heating dry platinic chloride (PtCl<sub>4</sub>) or gold chloride (AuCl<sub>3</sub>) in a hard glass tube.

$$\begin{aligned} &\text{PtCl}_{4} \xrightarrow{374^{\circ}\text{C}} &\text{PtCl}_{2} + \text{Cl}_{2} \xrightarrow{582^{\circ}\text{C}} &\text{Pt} + 2\text{Cl}_{2} \\ &2\text{AuCl}_{3} \xrightarrow{175^{\circ}\text{C}} &2\text{AuCl} + 2\text{Cl}_{2} \xrightarrow{185^{\circ}\text{C}} &2\text{Au} + \beta\text{Cl}_{2} \end{aligned}$$

**Manufacture:** Bulk of chlorine required for commercial purposes is obtained as a by-product in the manufacture of caustic soda by electrolysis of brine solution or in the manufacture of sodium by electrolysis of fused sodium chloride. These processes have already been described in Chapter 6 under caustic soda and sodium.

The other methods used for its manufacture are:

- (i) Weldon's process
- (ii) Deacon's process
- (iii) Nitrosyl chloride process

These chemical methods are bit costlier and only the nitrosyl chloride process is used these days to manufacture chlorine.

### (i) Weldon's Process

This process involves the heating of pyrolusite mineral (MnO<sub>2</sub>) with concentrated hydrochloric acid in stone-ware stills.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

The manganese chloride present in the waste liquor is converted into a product which can be used instead of fresh pyrolusite for oxidising more of hydrochloric acid. The manganese chloride solution is mixed with excess of lime and air is blown in the heated mixture. The following changes occur:

Calcium manganite settles down to the bottom as a dark coloured mud. This is used for oxidation of fresh quantities of hydrochloric acid.

$$CaMnO_3 + 6HCl \longrightarrow CaCl_2 + MnCl_2 + Cl_2 + 3H_2O$$

### (ii) Deacon's Process

This process is superior to Weldon's process. In this process, chlorine is obtained by the oxidation of HCl with air in presence of cupric chloride heated to 400°C.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

The catalytic action of cupric chloride can be explained with the following mechanism.

$$2CuCl_2 \xrightarrow{\quad High \, temp. \quad} Cu_2Cl_2 \, + \, Cl_2$$

$$2Cu_2Cl_2 \, + \, O_2(Air) \longrightarrow 2Cu_2OCl_2 \\ \hbox{Copper oxychloride}$$

$$Cu_2OCl_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$$

The cycle is then repeated, the gaseous products being steam and chlorine.

The mixture of air and hydrochloric acid, preheated to 220°C, is introduced into a chamber containing a number of shelves on which is placed pumice stone soaked in cupric chloride solution in HCl. This chamber is surrounded by a jacket in which hot gases at 450°C are passed.

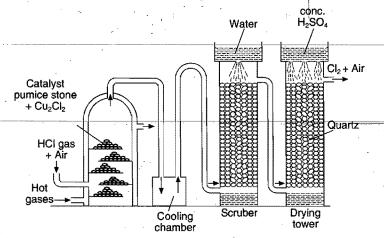


Fig. 12.5

The gaseous mixture which escapes from the top of the catalyst chamber consists Cl<sub>2</sub>, HCl, air and steam. It is freed from HCl by washing it with water in the washing tower and then dried by passing through the drying tower packed with pieces of flint and concentrated H<sub>2</sub>SO<sub>4</sub> flows down from the top. Finally, dry mixture of chlorine and air is obtained.

### (iii) Nitrosyl Chloride Process

In this process, common salt (NaCl) is treated with concentrated nitric acid, when a mixture of chlorine and nitrosyl chloride is evolved.

$$[NaCl + HNO_3 \longrightarrow NaNO_3 + HCl] \times 3$$

$$HNO_3 + 3HCl \longrightarrow NOCl + Cl_2 + 2H_2O$$

$$3NaCl + 4HNO_3 \longrightarrow 3NaNO_3 + NOCl + Cl_2 + 2H_2O$$

The gaseous mixture is oxidised with oxygen.

$$2NOC1 + O_2 \longrightarrow 2NO_2 + Cl_2$$

The gases are liquefied and chlorine distilled out. Nitrogen dioxide is absorbed in water in presence of oxygen to form nitric acid which can be used again.

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

**Storage and transportation of chlorine:** Chlorine is stored and transported in the liquid state. The liquid is stored in large steel tanks which are kept in heat-insulated cold storage rooms.

### Properties of Chlorine

**Physical:** (a) Chlorine is a yellowish green gas with a pungent suffocating smell. (b) It is heavier than air and oxygen. It is 2.5 times heavier than air. (c) It is poisonous in nature. It produces headache if inhaled in small quantity. It affects throat, nose and lungs. Large quantities prove fatal.

(d) It can be easily liquefied by cooling under pressure. The liquid chlorine is a yellow liquid (b.pt. -34.6°C). (e) It is fairly soluble in water. The aqueous solution is called chlorine water. It has yellow colour and smells of chlorine. At 0°C, crystals of chlorine hydrate Cl<sub>2</sub>·8H<sub>2</sub>O are formed.

Chemical: (a) Combustibility: Chlorine does not burn and also does not help in burning.

(b) Combination with elements: It combines with all the non-metals except nitrogen, oxygen, carbon and inert gases.

It combines with hydrogen in light (but not in dark) with explosion to form HCl. However, in presence of charcoal as a catalyst, the reaction is safe.

$$H_2 + Cl_2 \longrightarrow 2HCl$$

Arsenic, boron, sulphur, phosphorus (red), etc., combine with chlorine when heated.

$$\begin{array}{c} 2As + 3Cl_2 \longrightarrow 2AsCl_3 \\ & \text{Arsenic trichloride} \\ 2B + 3Cl_2 \longrightarrow 2BCl_3 \\ & \text{Boron trichloride} \\ 2S + Cl_2 \longrightarrow S_2Cl_2 \\ & \text{Disulphur dichloride} \\ 2P + 3Cl_2 \longrightarrow 2PCl_3 \\ \text{(Red)} \qquad \begin{array}{c} Phosphorus & trichloride \\ \end{array}$$

Yellow phosphorus readily catches fire in chlorine. Most of the metals directly react with chlorine to form corresponding chlorides. Alkali metals burn brilliantly in chlorine. Iron, copper, aluminium, magnesium, zinc, etc., when heated in chlorine form corresponding chlorides. A trace of moisture always catalyse the reaction.

$$\begin{array}{c} \text{2Na} + \text{Cl}_2 \longrightarrow \text{2NaCl} & ; \text{ 2Fe} + 3\text{Cl}_2 \longrightarrow \text{2FeCl}_3 \\ \text{2Al} + 3\text{Cl}_2 \longrightarrow \text{2AlCl}_3 & ; \text{ Cu} + \text{Cl}_2 \longrightarrow \text{CuCl}_2 \\ \text{ (or Al}_2\text{Cl}_6) & & \end{array}$$

$$Mg + Cl_2 \longrightarrow MgCl_2$$
 ;  $Zn + Cl_2 \longrightarrow ZnCl_2$ 

- (c) Affinity for hydrogen: It has great affinity for hydrogen. It decomposes several hydrogen compounds forming HCl.
  - (i) Turpentine burns in chlorine forming HCl and carbon.

$$C_{10}H_{16} + 8Cl_2 \longrightarrow 10C + 16HCl$$

(ii) It reacts with water in the presence of sunlight and forms  $O_2$ .

$$2H_2O + 2Cl_2 \longrightarrow 4HCl + O_2$$

Chlorine water loses its yellow colour on exposure to sunlight. This is due to the formation of HCl.

(iii) It reacts with ammonia under two conditions:

1. When ammonia in excess: The products are nitrogen and ammonium chloride.

$$2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl$$

$$[NH_3 + HCl \longrightarrow NH_4Cl] \times 6$$

$$8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

**2. When chlorine in excess:** The products are nitrogen trichloride and HCl.

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

(iv) It removes hydrogen from H<sub>2</sub>S.

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

(d) Oxidising and bleaching nature: In presence of moisture, chlorine acts as an oxidising and a bleaching agent. Chlorine reacts with water forming HCl and HClO (hypochlorous acid). HClO is not so stable and decomposes giving nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

$$\begin{array}{c} \text{Cl}_2 + \text{H}_2\text{O} & \longrightarrow \text{HCl} + \text{HClO} \\ & \text{HClO} & \longrightarrow \text{HCl} + \text{O} \\ \hline & \text{Cl}_2 + \text{H}_2\text{O} & \longrightarrow \text{2HCl} + \text{O} \end{array}$$

Coloured matter + Nascent oxygen - Colourless matter

The bleaching action is permanent. The delicate articles should not be bleached with chlorine.

1. It displaces bromine and iodine from bromides and iodides respectively.

$$2KBr + Cl2 \longrightarrow 2KCl + Br2 2KI + Cl2 \longrightarrow 2KCl + I2$$

2. Ferrous chloride/ferrous sulphate containing dilute H<sub>2</sub>SO<sub>4</sub>, is converted to ferric chloride/ferric sulphate.

$$2\text{FeCl}_2 + \text{Cl}_2 \longrightarrow 2\text{FeCl}_3$$
  
 $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{Cl}_2 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{HCl}$ 

3. Moist sulphur dioxide is oxidised to H<sub>2</sub>SO<sub>4</sub>.

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl_2$$

4. Sulphites are oxidised to sulphates.

$$Na_2SO_3 + H_2O + Cl_2 \longrightarrow Na_2SO_4 + 2HCl$$

5. Sulphur is precipitated from sodium thiosulphate.

$$Na_2S_2O_3 \,+\, H_2O \,+\, Cl_2 \longrightarrow \, Na_2SO_4 \,+\, 2HCl \,+\, S$$

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$$

(e) Action of alkalies: When passed into cold dilute solution of alkalies, it forms chlorides and hypochlorites.

$$\begin{array}{ccc} 2NaOH + Cl_2 & \longrightarrow NaCl + NaClO + H_2O \\ 2KOH + Cl_2 & \longrightarrow KCl + KClO + H_2O \\ 2Ca(OH)_2 + 2Cl_2 & \longrightarrow CaCl_2 + Ca(ClO)_2 + 2H_2O \\ Cold \ and \ dilute \end{array}$$

With hot concentrated alkali solutions, chlorates are formed.

$$6$$
NaOH +  $3$ Cl<sub>2</sub>  $\longrightarrow$   $5$ NaCl + NaClO<sub>3</sub> +  $3$ H<sub>2</sub>  
 $6$ KOH +  $3$ Cl<sub>2</sub>  $\longrightarrow$   $5$ KCl + KClO<sub>3</sub> +  $3$ H<sub>2</sub>O  
 $6$ Ca(OH)<sub>2</sub> +  $6$ Cl<sub>2</sub>  $\longrightarrow$   $5$ CaCl<sub>2</sub> + Ca(ClO<sub>3</sub>)<sub>2</sub> +  $6$ H<sub>2</sub>O  
Hot and conc.

However, when chlorine is passed over dry slaked lime, bleaching powder is obtained.

$$\begin{array}{c} Ca(OH)_2 + Cl_2 & \longrightarrow CaOCl_2 \cdot H_2O \\ \text{Slaked lime} & \text{Bleaching powder} \end{array}$$

**(f) Addition reactions:** Chlorine forms addition compounds with SO<sub>2</sub>, CO and unsaturated hydrocarbons.

$$SO_2 + Cl_2 \xrightarrow{} SO_2Cl_2$$
;  $CO + Cl_2 \xrightarrow{} COCl_2$   
Sulphuryl chloride (Phosgene)

Phosgene is highly poisonous gas.

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$
Ethylene chloride

### Uses of Chlorine

It is used: (i) in the manufacture of bleaching powder, chlorates, hypochlorites, hydrochloric acid, chloroform, carbon tetrachloride and a number of synthetic organic compounds. (ii) in the purification of drinking water. (iii) as a bleaching agent for cotton fabrics, paper and rayon. (iv) in the extraction of gold and platinum. (v) as an oxidising agent. (vi) as a germicide and disinfectant. (vii) for the manufacture of poisonous gases like phosgene (COCl<sub>2</sub>), tear gas (CCl<sub>3</sub>·NO<sub>2</sub>) and mustard gas (Cl—C<sub>2</sub>H<sub>4</sub>—S—C<sub>2</sub>H<sub>4</sub>—Cl).

### 12.5 BROMINE

Bromine was discovered in 1826 by the French chemist **Balard** in the mother liquor left after the crystallisation of common salt from sea water. The name bromine was given due to its bad and pungent odour (Greek: *Bromos*, a stench).

**Occurrence:** It is never found in free state in nature. The chief sources of bromine are:

- (i) Sea water contains bromides such as NaBr, KBr, MgBr<sub>2</sub>, CaBr<sub>2</sub>, etc., in minute amounts.
- (ii) The mother liquor left after the crystallisation of potassium chloride from carnallite, KCl, MgCl<sub>2</sub>·6H<sub>2</sub>O (found in Stassfurt, Germany) contains some bromocarnallite, KBr·MgBr<sub>2</sub>·6H<sub>2</sub>O.
- (iii) The bromides such as NaBr, MgBr<sub>2</sub>, etc., are found in small amounts in mineral springs and salt lakes.
  - (iv) Bromargyrite: a mineral, AgBr.

**Preparation:** The following reactions can be used for its preparation.

(i) By passing chlorine through the solution of potassium or magnesium bromide.

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$
  
 $MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$ 

(ii) By adding hydrochloric acid to the mixture containing potassium bromide and potassium bromate.

$$5KBr + KBrO_3 + 6HCl \longrightarrow 6KCl + 3Br_2 + 3H_2O$$

(iii) By heating mixture of potassium bromide and manganese dioxide with conc. H<sub>2</sub>SO<sub>4</sub>.

$$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + O$$
  
 $[KBr + H_2SO_4 \longrightarrow KHSO_4 + HBr] \times 2$   
 $2HBr + O \longrightarrow H_2O + Br_2$ 

$$2KBr + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + Br_2 + 2H_2O$$

This reaction is commonly used in the laboratory for the preparation of bromine. The apparatus used has been shown in Fig. 12.6.

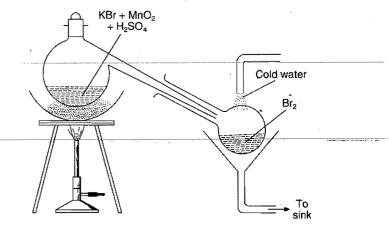


Fig. 12.6

A mixture consisting 5 g of potassium bromide and 14 g of manganese dioxide is taken in a glass retort. 30 mL concentrated sulphuric acid to which 180 mL of water has been added, is poured over the mixture in the retort. The contents are heated slowly. The reddish brown vapours of bromine are evolved. These vapours are collected in a receiver which is cooled under cold water. Bromine vapours condense to give a dark red liquid.

Since the bromine vapours are poisonous, the preparation is either carried out in a fuming cup board or in a well ventillated laboratory.

### Manufacture

1. From carnallite mother liquor: The mother liquor left after the crystallisation of potassium chloride from carnallite contains about 0.25% of bromine as magnesium bromide and potassium bromide.

The hot mother liquor is made to flow down a tower packed with earthen-ware balls (Fig. 12.7). A current of chlorine and steam is introduced from the bottom of the tower. The vapours of bromine set free are condensed in a condenser.

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$$

The vapours which do not condense are allowed to pass through a tower packed up with moist iron filings, forming iron bromides.

$$\begin{array}{ccc} Fe + Br_2 & \longrightarrow FeBr_2 \\ 3FeBr_2 + Br_2 & \longrightarrow Fe_3Br_8 \\ & & \text{Ferroso-ferric bromide} \end{array}$$

This is used for manufacture of potassium bromide.

The bromine so obtained contains chlorine and iodine as impurities. It is purified by distilling it with potassium bromide and zinc oxide. The bromide reacts with chlorine while zinc oxide reacts with iodine.

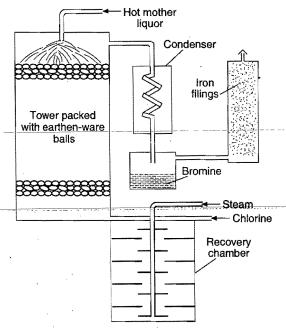


Fig. 12.7

**2. From sea water:** Sea water is the most important source of commercial bromine.

The sea water is slightly acidified and then treated with chlorine to liberate the bromine.

$$Cl_2 + Bromides \longrightarrow Chlorides + Bromine$$
(Sea water)

The evolved bromine is blown out by means of a current of air. The air carrying the bromine vapours are passed through absorption towers down which a sodium carbonate solution is sprayed. The bromide combines forming sodium bromate and sodium bromide.

$$3Na_2CO_3 + 3Br_2 \longrightarrow NaBrO_3 + 5NaBr + 3CO_2$$

The solution containing bromide and bromate is distilled with H<sub>2</sub>SO<sub>4</sub> to recover bromine.

$$[2NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2HBr] \times 5$$
  
 $2NaBrO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HBrO_3$   
 $[HBrO_3 + 5HBr \longrightarrow 3Br_2 + 3H_2O] \times 2$ 

$$10\text{NaBr} + 2\text{NaBrO}_3 + 6\text{H}_2\text{SO}_4 \longrightarrow 6\text{Na}_2\text{SO}_4 + 6\text{Br}_2 + 6\text{H}_2\text{O}$$
 or  $5\text{NaBr} + \text{NaBrO}_3 + 3\text{H}_2\text{SO}_4 \longrightarrow 3\text{Na}_2\text{SO}_4 + 3\text{Br}_2 + 3\text{H}_2\text{O}$  The vapours are condensed.

### **圏 Properties**

**Physical:** (a) It is a reddish brown, heavy mobile liquid. Its density is 3.2. It boils at 58.5°C and freezes at -7.2°C to

a yellowish brown solid. (b) It has irritating bad odour. The vapours attack the eyes and mucous membrane of nose and throat. It brings blisters on the skin which take a very long time to heal. It is poisonous. (c) It is fairly soluble in water (about 3.6% at 20°C). The solution is termed bromine water. A saturated solution of bromine when cooled in a freezing mixture gives bromine hydrate, Br<sub>2</sub>·8H<sub>2</sub>O. (d) It is more soluble in chloroform, carbon tetrachloride, benzene, carbon disulphide, etc. The colour of solution is usually reddish brown.

Chemical: In chemical behaviour, bromine closely resembles chlorine.

### (a) Combination with elements: •

(i) Bromine reacts directly with hydrogen, though less readily than chlorine. The reaction,

$$H_2 + Br_2 \longrightarrow 2HBr$$

is slightly reversible. It combines with hydrogen at 200°C or at room temperature in presence of platinum as catalyst.

(ii) It combines with sulphur, phosphorus, arsenic, etc.

$$\begin{array}{c} 2P + 3Br_2 \longrightarrow 2PBr_3 \\ 2As + 3Br_2 \longrightarrow 2AsBr_3 \\ 2B + 3Br_2 \xrightarrow{Red \, heat} 2BBr_3 \end{array}$$

(iii) It combines directly with many metals.

$$2Na + Br_2 \longrightarrow 2NaBr$$
 (Slow reaction)  
 $2K + Br_2 \longrightarrow 2KBr$  (Fast reaction)  
 $2Al + 3Br_2 \longrightarrow 2AlBr_3$  (Violent reaction)

Zinc reacts in presence of moisture with bromine.

$$Zn + Br_2 \longrightarrow ZnBr_2$$

**(b) Oxidising action:** Bromine is a good oxidising agent. It ordinarily does not react with water but in presence of an oxidisable substance it forms hydrogen bromide and oxygen with water.

$$Br_2 + H_2O \longrightarrow 2HBr + O$$
 $X + O \longrightarrow XO$ 
Oxidisable substance

(i) It oxidises SO<sub>2</sub> into sulphuric acid.

$$SO_2 + Br_2 + 2H_2O \longrightarrow 2HBr + H_2SO_4$$

(ii) It oxidises sulphites into sulphates.

$$Na_2SO_3 + Br_2 + H_2O \longrightarrow Na_2SO_4 + 2HBr$$

(iii) It oxidises arsenites into arsenates.

$$Na_3AsO_3 + Br_2 + H_2O \longrightarrow Na_3AsO_4 + 2HBr$$

(iv) It oxidises thiosulphate into sulphate.

$$Na_2S_2O_3 + Br_2 + H_2O \longrightarrow Na_2SO_4 + S + 2HBr$$

(v) Sulphur is formed by oxidation of hydrogen sulphide.

$$H_2S + Br_2 \longrightarrow 2HBr + S$$

(vi) Iodine is liberated from iodides.

$$2KI + Br_2 \longrightarrow 2KBr + I_2$$

(c) Action with alkalies: The action of bromine on alkalies is similar to that of chlorine, a hypobromite with a cold dilute solution and a bromate with a hot solution are formed.

$$\begin{array}{c} 2KOH + Br_2 \longrightarrow KBr + KBrO + H_2O \\ \text{(Dil. and cold)} & \text{Pot. hypobromite} \\ \end{array}$$

$$6KOH + 3Br_2 \longrightarrow 5KBr + KBrO_3 + 3H_2O$$
(Conc. and hot) Pot. bromate

$$6Ba(OH)_2 + 6Br_2 \longrightarrow 5BaBr_2 + Ba(BrO_3)_2 + 6H_2O$$
(Conc. and hot)

Barium

$$3Na_2CO_3 + 3Br_2 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$$
 (Conc. and hot)

However, with slaked lime (dry) it forms a compound similar to bleaching powder.

$$Ca(OH)_2 + Br_2 \longrightarrow CaOBr_2 + H_2O$$
Slaked lime
(Dry)

(d) Action of ammonia: It is similar to that of chlorine.

$$8NH_3 + 3Br_2 \longrightarrow 6NH_4Br + N_2$$

**(e) Action of organic compounds:** It forms addition compounds with unsaturated compounds and substituted products with the saturated compounds.

$$C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$$
  
 $CH_4 + Br_2 \longrightarrow CH_3Br + HBr$ 

- (f) Bleaching action: The bleaching action of bromine is weaker than that of chlorine. The bleaching action is due to its oxidising property.
- (g) Action of mercuric oxide: Bromine water reacts with mercuric oxide to form mercury oxybromide.

$$2\text{HgO} + 2\text{Br}_2 + \text{H}_2\text{O} \longrightarrow \text{HgBr}_2 \cdot \text{HgO} + 2\text{HBrO}$$

Mercury oxybromide

However, on passing bromine vapours over dry HgO at 60°C, bromine monoxide is obtained.

$$HgO + 2Br_2 \longrightarrow Br_2O + HgBr_2$$

### Uses of Bromine

- (i) The chief use of bromine is in the manufacture of ethylene bromide (C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>) which is extensively employed as a component of anti-knock gasoline.
- (ii) It is used in the manufacture of NaBr and KBr (used in medicine as sedative), and certain organic dyes.
- (iii) Bromine water is used in organic chemistry to test the unsaturation of organic compounds.
  - (iv) It is used as germicide.
- (v) It is employed as an oxidising agent and in organic synthesis.

### 12.6 IODINE

Iodine was discovered by **Courtois** in 1812 from the ashes of sea-weeds. Gay-Lussac established its elementary nature and named it iodine on account of the violet colour of its vapours (Greek; *Ioeides* = violet).

**Occurrence:** Iodine never occurs free in nature. In combined state, it occurs as iodides and sodium iodate. Traces of compounds of this element are found in plants and animals, in certain minerals and in sea water.

There are two main sources of iodine:

- (i) Certain deep sea-weeds (Laminaria species). These plants contain 0.5% of iodine in their ashes (known as kelp) in the form of iodides.
- (ii) Caliche or crude chile saltpetre which contains about 0.2% of NaIO<sub>3</sub> (sodium iodate).

The less important sources of iodine are:

- (i) Sodium, potassium and magnesium iodides in very small amounts are found in ores of lead and dolomite.
- (ii) Sea water contains iodides and organic compounds containing iodine.
  - (iii) Thyroxine which is present in thyroid gland.
  - (iv) Oil-well brines contain NaI.

**Preparation:** The following reactions can be applied for the preparation of iodine:

(i) By passing chlorine through potassium iodide solution.

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

(ii) By adding potassium iodide solution to copper sulphate solution.

$$\begin{array}{c} \text{CuSO}_4 \,+\, 2\text{KI} \longrightarrow & \text{CuI}_2 \,+\, \text{K}_2\text{SO}_4 \\ 2\text{CuI}_2 \longrightarrow & \text{Cu}_2\text{I}_2 \,+\, \text{I}_2 \\ \text{Cupric} & \text{Cuprous} \\ \text{indide} & \text{indide} \end{array}$$

(iii) By adding conc. sulphuric acid to a mixture of sodium/potassium iodide and sodium/potassium iodate.

$$\begin{aligned} [\text{NaI} + \text{H}_2\text{SO}_4 & \longrightarrow \text{NaHSO}_4 + \text{HI}] \times 5 \\ \text{NaIO}_3 + \text{H}_2\text{SO}_4 & \longrightarrow \text{NaHSO}_4 + \text{HIO}_3 \\ \text{HIO}_3 + 5\text{HI} & \longrightarrow 3\text{H}_2\text{O} + 3\text{I}_2 \end{aligned}$$

$$\overline{\text{NaIO}_3 + 5\text{NaI} + 6\text{H}_2\text{SO}_4 \longrightarrow 6\text{NaHSO}_4 + 3\text{H}_2\text{O} + 3\text{I}_2}$$

(iv) By adding an oxidising agent such as hydrogen peroxide, ozone, acidified potassium permanganate or acidified potassium dichromate to potassium iodide.

$$2KI + H_2O_2 \longrightarrow 2KOH + I_2$$

(v) By reacting sodium iodate with sodium hydrogen sulphite.

$$2NaIO_3 + 5NaHSO_3 \longrightarrow 3NaHSO_4 + 2Na_2SO_4 + I_2 + H_2O_3$$

(vi) By heating mixture of potassium iodide and manganese dioxide with conc. H<sub>2</sub>SO<sub>4</sub>.

$$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$
 $MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + O$ 
 $2HI + O \longrightarrow H_2O + I_2$ 

$$2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2$$

Iodine, in the laboratory, is usually prepared by this reaction. The following materials are taken in a beaker, KI (3.5 g),  $MnO_2$  (7.0 g) and 6N  $H_2SO_4$  (100 mL).

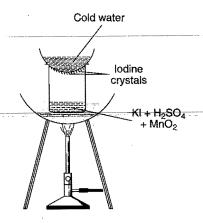


Fig. 12.8

The contents are heated and the vapours of evolved iodine are condensed on a watch glass, cooled by ice as shown in Fig. 12.8.

### Manufacture

(i) From sea-weeds: The sea-weeds are collected, dried and burnt in shallow pits. The ash left is called **kelp.** The ash is extracted with hot water which dissolves out chlorides, carbonates, sulphates and iodides of sodium and potassium.

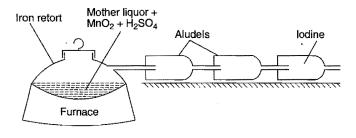


Fig. 12.9

The solution on concentration and cooling separates out chlorides, sulphates and carbonates while iodides remain in solution. The solution is mixed with manganese dioxide and concentrated sulphuric acid in iron retorts. Iodine is liberated and condensed in series of earthen-ware receivers known as *Aludels*.

$$[NaI + H2SO4 \longrightarrow NaHSO4 + HI] \times 2$$

$$MnO2 + H2SO4 \longrightarrow MnSO4 + H2O + O$$

$$2HI + O \longrightarrow H2O + I2$$

$$2 NaI + MnO_2 + 3H_2SO_4 \longrightarrow 2 NaHSO_4 + MnSO_4 + H_2O + I_2$$

Pure iodine is obtained by sublimation.

(ii) From caliche: Chile saltpetre is dissolved in water. The solution is concentrated and cooled to separate sodium nitrate crystals. The mother liquor is treated with a calculated amount of sodium hydrogen sulphite\* solution to precipitate out iodine.

$$[NaIO_3 + 3NaHSO_4 \longrightarrow NaI + 3NaHSO_4] \times 5$$

$$NaIO_3 + NaHSO_4 \longrightarrow Na_2SO_4 + HIO_3$$

$$[NaI + NaHSO_4 \longrightarrow Na_2SO_4 + HI] \times 5$$

$$HIO_3 + 5HI \longrightarrow 3H_2O + 3I_2$$

$$6$$
NaIO<sub>3</sub>+  $15$ NaHSO<sub>3</sub>  $\longrightarrow$   $9$ NaHSO<sub>4</sub>+  $6$ Na<sub>2</sub>SO<sub>4</sub>+  $3$ H<sub>2</sub>O +  $3$ I<sub>2</sub>  
or  $2$ NaIO<sub>3</sub>+  $5$ NaHSO<sub>3</sub>\*  $\longrightarrow$   $3$ NaHSO<sub>4</sub>+  $2$ Na<sub>2</sub>SO<sub>4</sub>+  $H$ <sub>2</sub>O+I<sub>2</sub>

**Purification:** Commercial iodine obtained in the above processes may contain iodine chloride (ICl), iodine bromide (IBr) and iodine cyanide (ICN) which are difficult to be removed by sublimation. The impure iodine is distilled with potassium iodide which removes the impurities and pure iodine vapours are condensed.

$$KI + ICI \longrightarrow KCl + I_2$$
  
 $KI + IBr \longrightarrow KBr + I_2$   
 $KI + ICN \longrightarrow KCN + I_2$ 

KCl, KBr and KCN are non-volatile substances.

### Properties

**Physical:** (a) It is a black (dark violet) shining solid, *i.e.*, it has metallic lustre. (b) It melts at 114°C and boils at 184°C. However, it sublimes rapidly below melting point giving violet coloured vapours. (c) Iodine produces stains on skin. Its vapours are pungent and irritating and very dangerous to inhale. (d) Its specific gravity is 4.98. It is diatomic in nature and when heated at 1700°C, it is converted into atomic form.

$$I_2 \stackrel{1700^{\circ}C}{\longleftarrow} I + I$$

(e) It is slightly soluble in water giving a light brown solution. Its solubility increases in water in presence of potassium iodide due to formation of potassium tri-iodide. KI<sub>3</sub> easily breaks down and thus the solution has all the properties of free iodine.

$$KI + I_2 \rightleftharpoons KI_3$$

(f) It is soluble in many organic solvents such as chloroform, carbon tetrachloride, alcohol, ether and carbon disulphide. The solution in CS<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub> is violet in colour.

Chemical: Iodine is chemically less reactive in comparison to chlorine and bromine.

<sup>\*</sup>NaHSO<sub>3</sub> if present in excess, HI is produced, NaHSO<sub>3</sub> + I<sub>2</sub> + H<sub>2</sub>O ---- NaHSO<sub>4</sub> + 2HI

(a) Combination with elements: It combines directly with many elements.

$$H_{2} + I_{2} \xrightarrow{\text{Heat}} 2HI$$

$$2P + 3I_{2} \xrightarrow{\text{Heat}} 2PI_{3}$$

$$2K + I_{2} \longrightarrow 2KI$$

$$2Fe + 3I_{2} \xrightarrow{\text{Heat}} 2FeI_{3}$$

**(b) Oxidising properties:** It is a weak oxidising agent. The following reactions show its oxidising nature.

(i) 
$$H_2S + I_2 \longrightarrow 2HI + S$$

(ii) 
$$SO_2 + I_2 + 2H_2O \longrightarrow H_2SO_4 + 2HI$$

(iii) 
$$Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + 2HI$$

(iv) 
$$Na_3AsO_3 + I_2 + H_2O \longrightarrow Na_3AsO_4 + 2HI$$

(v) 
$$2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{I}_2 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{HI}$$

(c) Reaction with alkalies: Iodine reacts with cold dilute solution of NaOH forming hypoiodite. The colour of the solution becomes faint yellow. However, hypoiodite undergoes hydrolysis forming HIO.

$$\begin{array}{c} \text{2NaOH} + \text{I}_2 \longrightarrow \text{NaIO} + \text{NaI} + \text{H}_2\text{O} \\ \hline \text{NaIO} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{HIO} \\ \hline \hline \text{NaOH} + \text{I}_2 \longrightarrow \text{NaI} + \text{HIO} \\ \hline \text{Hypoiodous acid} \\ \end{array}$$

Iodine when heated with concentrated alkali solution, iodide and iodate are formed. The colour of iodine disappears.

$$6\text{NaOH} + 3\text{I}_2 \longrightarrow \underbrace{5\text{NaI} + \text{NaIO}_3}_{\text{Colourless}} + 3\text{H}_2\text{O}$$

(d) Iodine does not displace chlorine and bromine from chlorides and bromides, respectively but it displaces them from their oxy salts.

$$2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2$$
  
 $2KBrO_3 + I_2 \longrightarrow 2KIO_3 + Br_2$ 

**(e) Reaction with sodium thiosulphate:** Iodine solution is decolourised by sodium thiosulphate (hypo) as sodium tetrathionate and sodium iodide are formed. Both are colourless and soluble.

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$
 Sodium thiosulphate Sodium tetrathionate

This reaction is involved in iodometric titrations in presence of starch indicator. (f) Action of NH<sub>3</sub>: Iodine forms a mild explosive with ammonia.

$$2NH_3 + 3I_2 \longrightarrow NI_3 \cdot NH_3 + 3HI$$
  
Explosive  
 $8NI_3 \cdot NH_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$ 

- (g) Reaction with strong oxidising agents: Strong oxidising agents convert iodine to iodic acid (HIO<sub>3</sub>).
  - (i) With conc. HNO<sub>3</sub>.

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

(ii) With ozone.

$$I_2 + H_2O + 5O_3 \longrightarrow 2HIO_3 + 5O_2$$

(iii) With chlorine water.

$$I_2 + 5Cl_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$$

(h) Reaction with freshly precipitated mercuric oxide: Iodine forms hypoiodous acid with mercuric oxide.

$$2HgO + 2I_2 + H_2O \longrightarrow HgI_2 \cdot HgO + 2HIO$$

(i) Iodine when warmed with alcohol and alkali forms iodoform.

$$C_2H_5OH + 6KOH + 4I_2 \longrightarrow CHI_3 + HCOOK + 5KI + 5H_2O$$

- (j) Reaction with chlorine: When chlorine is passed over iodine, at first iodine monochloride, ICl (dark liquid) and finally iodine trichloride, ICl<sub>3</sub> (yellow solid) is formed.
- (k) Reaction with starch: Iodine turns starch solution blue. This is one of the tests of iodine.
- (1) Action on unsaturated organic compounds: Addition products are formed with unsaturated organic compounds.

$$C_2H_4 + I_2 \longrightarrow C_2H_4I_2$$

#### Uses of lodine

- (a) It is used in medicine, e.g., tincture of iodine  $[\frac{1}{2}$  oz. iodine,  $\frac{1}{4}$  oz. KI and 1 pint rectified spirit] and iodex as antiseptic and analgesic. Solutions of iodine in KI are used in the treatment of goitre.
- (b) It is used in the preparation of iodoform, iodides, dyes, etc.
  - (c) It is used in the analytical chemistry.
- (d) It is used in the preparation of photosensitive papers, films and plates.

## COMPARISON OF HALOGENS (F2, Cl2, Br2 and l2)

S.No.	Property	Fluorine	Chlorine	Bromine	Iodine
1.	Physical state at	Gas ,	Gas	Liquid	Solid
	ordinary	,			
	temperatures		·		
2.	Colour	Pale greenish yellow	Pale greenish yellow	Reddish brown	Violet .
3.	Solubility in water	Decomposes water to form	Soluble to form OCl	Less soluble than chlorine	Less soluble than bromine
		HF, O <sub>2</sub> and O <sub>3</sub>			
4.	Density of the solid	1.3	1.9	3.4	4.93
	$(g mL^{-1})$			'	
5.	Boiling point (°C)	-187	-34.6	58.78	183
6.	Electronegativity	4.0	3.0	2.8	2.5
	(Pauling scale)				
7.	Chemical reactivity	Highly reactive	Quite active	Less active than chlorine	Less active than bromine
8.	Reaction with	_			
	(i) hydrogen	Combines explosively even	Explosive in light, slow in	Only on heating	On heating and in presence
	-	in the dark	dark		of a catalyst
	(ii) water	Decomposes forming HF,	Forms chlorine hydrate	Decomposes slowly in	No action
- 4 .4	TE SHINE STREET	O <sub>2</sub> and O <sub>3</sub>	with ice-cold water	presence of light forming	
			Decomposes slowly	HBr and HBrO or HBr and	
			forming HCl and HClO or	$O_2$	
		,	HCl and O <sub>2</sub>	_	
	(iii) alkalies	With dilute alkalies, F <sub>2</sub> O	Forms chlorides and hypo-	Same as chlorine	Same as chlorine
	•	and alkali fluorides are	chlorites with cold dil	$2NaOH + Br_2 \longrightarrow$	$2NaOH + I_2 \longrightarrow$
		formed. With conc. alkalies,	alkali solution. Chlorides	dil.	NaI + NaIO + H <sub>2</sub> O
		alkali fluorides and O2 are	and chlorates are formed	NaBr + NaBrO + H <sub>2</sub> O	6NaOH + 3I <sub>2</sub> →
		formed	with hot conc. solutions	$6$ NaOH + $3$ Br <sub>2</sub> $\longrightarrow$	$5NaI + NaIO_3 + 3H_2O$
		$2\text{NaOH} + 2\text{F}_2 \xrightarrow{\text{dil.}}$	2NaOH (dil.) + Cl <sub>2</sub> →	conc.	
		$F_2O + Na_2F_2 + H_2O$	NaCl + NaClO + H <sub>2</sub> O	5NaBr + NaBrO <sub>3</sub> + 3H <sub>2</sub> O	
			6NaOH + 3Cl <sub>2</sub> → 5NaCl +		
			conc.		,
		$4\text{NaOH} + 2\text{F}_2 \xrightarrow{\text{conc.}}$	NaClO <sub>3</sub> + 3H <sub>2</sub> O		
	*	$2Na_2F_2 + 2H_2O + O_2$			
	(iv) halides	Displaces other halogens	Displaces Br <sub>2</sub> and I <sub>2</sub> from	Displaces I <sub>2</sub> from iodides	
			bromides and iodides		
	(v) metals	Reacts with all metals to	Reacts with almost all	Many metals are acted upon	React only with few metals
		form fluorides	metals forming chlorides	and bromides are formed	to form iodides
•	(vi) non-metals	Combines with all non-	Combines with many non-	Combines with many non-	Combines with only few
	,	metals except N2, O2 and	metals (except C, N <sub>2</sub> , O <sub>2</sub>	metals	non-metals such as P, As,
		lower inert gases	and inert gases)		etc.
9.	Oxidising nature	Very strong oxidising agent	Strong oxidising agent	Good oxidising agent	Mild oxidising agent
10.	Bleaching action	Destroys the reducible	Bleaches vegetable colours	Mild bleaching agent	
,		coloured substance	easily		

## 12.7 HALOGEN ACIDS OR HYDRACIDS

All the halogens combine with hydrogen and form the covalent hydrides of HX type (X = F, Cl, Br or I). These hydrides are called hydracids or halogen acids.

Hydrogen fluoride (HF)

Hydrogen chloride (HCl)

Hydrogen bromide (HBr)

Hydrogen iodide (HI)

## Preparation (HCI, HBr and HI)

(i) By the direct combination of elements: Hydrogen chloride (HCl) is formed by burning chlorine in excess of hydrogen.

$$H_2 + Cl_2 \longrightarrow 2HCl$$

HBr can be prepared by passing a mixture of H<sub>2</sub> and Br<sub>2</sub> over a platinum spiral heated to redness by an electric current.

$$H_2 + Br_2 \xrightarrow{Pt} 2HBr$$

HI can also be prepared in small quantities by passing hydrogen and iodine vapours over red hot fine platinum.

$$H_2 + I_2 \xrightarrow{Pt} 2HI$$

(ii) By heating a halide with acid: Hydrogen chloride is prepared by heating sodium chloride with concentrated sulphuric acid.

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$

HBr and HI cannot be prepared by heating bromides and iodides with concentrated H<sub>2</sub>SO<sub>4</sub> because HBr and HI are strong reducing agents and reduce H<sub>2</sub>SO<sub>4</sub> to SO<sub>2</sub> and get themselves oxidised to bromine and iodine, respectively.

$$KBr + H_2SO_4 \longrightarrow KHSO_4 + HBr$$
 $KI + H_2SO_4 \longrightarrow KHSO_4 + HI$ 
 $H_2SO_4 + 2HBr \longrightarrow SO_2 + Br_2 + 2H_2O$ 
 $H_2SO_4 + 2HI \longrightarrow SO_2 + I_2 + 2H_2O$ 

Thus, HBr and HI are prepared by heating bromides and iodides respectively with conc. orthophosphoric acid.

$$3KBr + H_3PO_4 \longrightarrow K_3PO_4 + 3HBr$$
  
 $3KI + H_3PO_4 \longrightarrow K_3PO_4 + 3HI$ 

(iii) HBr and HI can be prepared by hydrolysis of corresponding phosphorus trihalides.

$$2P + 3Br_2 \longrightarrow 2PBr_3$$
  
 $2P + 3I_2 \longrightarrow 2PI_3$   
 $PBr_3 + 3H_2O \longrightarrow H_3PO_3 + 3HBr$   
 $PI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HI$ 

**Hydrogen fluoride:** It is an associated molecule and is represented by formula,  $H_2F_2$ .

Pure anhydrous hydrogen fluoride is obtained by heating potassium hydrogen fluoride (dry) in a platinum retort.

$$2KHF_2 \longrightarrow K_2F_2 + H_2F_2$$

The vapours are condensed in a platinum condenser and collected in a platinum receiver. In place of platinum, lead apparatus can also be used.

The aqueous solution of  $H_2F_2$  can be obtained by heating calcium fluoride with 90% conc. sulphuric acid in a lead retort. The vapours are condensed in a strongly cooled lead receiver. Aqueous acid of about 40% strength can be obtained by passing the vapours through water in a lead receiver.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2F_2$$

The aqueous solution of  $H_2F_2$  is kept in qutta-percha bottles when dilute and in wax bottles when concentrated. The anhydrous acid is stored in well cooled platinum, gold or silver vessels or steel cylinders.

#### **Properties**

(i) Physical state: Except H<sub>2</sub>F<sub>2</sub>, other hydrogen halides

are gases. They fume in air and have pungent odour. These are colourless. All are heavier than air and can be liquefied to colourless liquids.

Their melting and boiling points increase with increase in atomic mass of the halogen. The low values are due to covalent nature.

	HCl .	$\mathbf{HBr}$	HI
Melting point (°C)	-111	-86	-50.8
Boiling point (°C)	-85	-67	-35.5

 $H_2F_2$  is a liquid with boiling point 19.5°C. This behaviour is due to association of HF molecules through hydrogen bonding.

(ii) Constant boiling mixtures: These are fairly soluble in water. They form constant boiling mixtures with water called azeotrope.

Hydrogen halide	Composition	Boiling point (°C
$H_2F_2$	36%	120
HCl	20.4%	110
HBr	47%	126
HI	57%	. 127

(iii) Stability: The bond strength H—X decreases from HF to HI. Thus, HF is most stable while HI is least stable. The decrease in stability is due to decrease in electronegativity from F to I. This is also observed in the values of dissociation energy of H—X bond.

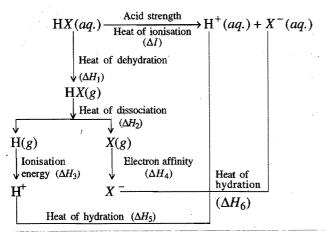
	H-F	H—Cl	H—Br	H—I
Dissociation				
energy (kcal mol <sup>-1</sup> )	136	105	86	70

HF and HCl are stable upto 1200°C, HBr dissociates slightly and HI dissociates considerably (20%) at 440°C.

(iv) Acid strength: Hydrogen halides in the gaseous state are essentially covalent. In aqueous solutions, however, they ionise and act as acids. HF is only slightly ionised but HCl, HBr and HI are almost completely ionised, *i.e.*, the relative strength increases from HF to HI. HF is the weakest acid and HI is the strongest acid. On the basis of electronegativity, this appears to be rather surprising. [The electronegativity difference suggests that HF should be strongest and HI should be weakest acid.] The increase in strength is reflected from the dissociation constant values,  $K_a$ , of these hydrogen halides.

HF HCl HBr HI 
$$K_a = 7 \times 10^{-4}$$
  $7 \times 10^{8}$   $7 \times 10^{10}$   $7 \times 10^{11}$ 

The anomalous behaviour is explained with the help of **Born-Haber cycle.** The various factors which determine the strengths of the acids in aqueous medium can be represented in the form of Born-Haber cycle, as shown below:



Summation of all energy terms will be equal to  $\Delta I$ .  $\Delta I = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - (\Delta H_5 + \Delta H_6)$ 

The values of  $\Delta I$  for various halogen acids as calculated are given below:

$$HF$$
 HCI HBr HI  $\Delta I$  (kJ mol<sup>-1</sup>) -12 -59 -63 -57

The larger the negative value  $\Delta I$ , the greater is the feasibility of ionisation reaction and hence the greater is the strength of the halogen acid.

The value of HF is small compared to other acids, hence HF is the weakest acid. The values also explain the gradual increasing strength of HCl and HBr but fail to explain the strength of HI. This discrepency is explained on the basis of entropy changes ( $\Delta S$ ) accompanying the process of ionisation.

The lower strength of HF is largely due to its high bond dissociation energy as the bond length is very small (1.01 Å).

(v) Reducing nature: The reducing nature increases from HF to HI as the stability decreases from HF to HI. HF does not show reducing nature. It cannot be oxidised even by strong oxidising agents. HI is the strongest reducing agent. Its aqueous solution gets oxidised even by atmospheric oxygen.

$$4HI + O_2 \longrightarrow 2H_2O + 2I_2$$

The reducing action can also be explained on the basis of increasing size of the halide ions from  $F^-$  to  $I^-$ . The bigger ion can lose electron easily.

HCl can be oxidised by strong oxidising agents like MnO<sub>2</sub>, KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, PbO<sub>2</sub>, Pb<sub>3</sub>O<sub>4</sub>, etc. (see reactions in section 12.4).

HBr acts stronger reducing agent than HCl. It can be oxidised by  $H_2SO_4$  and atmospheric oxygen.

$$H_2SO_4 + 2HBr \longrightarrow SO_2 + Br_2 + 2H_2O$$
  
 $4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$ 

HI is the strongest reducing agent.

It reduces  $H_2SO_4$  to  $SO_2$ , S and  $H_2S$ , nitric acid to  $NO_2$ , nitrous acid to NO,  $FeCl_3$  to  $FeCl_2$ , cupric salt to cuprous salt, etc.

$$H_2SO_4 + 2HI \longrightarrow SO_2 + I_2 + 2H_2O$$

$$\begin{array}{c} \text{H}_2\text{SO}_4 + 6\text{HI} \longrightarrow \text{S} + 3\text{I}_2 + 4\text{H}_2\text{O} \\ \text{H}_2\text{SO}_4 + 8\text{HI} \longrightarrow \text{H}_2\text{S} + 4\text{I}_2 + 4\text{H}_2\text{O} \\ 2\text{HNO}_3 + 2\text{HI} \longrightarrow 2\text{NO}_2 + 2\text{H}_2\text{O} + \text{I}_2 \\ 2\text{HNO}_2 + 2\text{HI} \longrightarrow 2\text{NO} + 2\text{H}_2\text{O} + \text{I}_2 \\ 2\text{FeCl}_3 + 2\text{HI} \longrightarrow 2\text{FeCl}_2 + \text{I}_2 + 2\text{HCl} \\ 2\text{CuSO}_4 + 4\text{HI} \longrightarrow \text{Cu}_2\text{I}_2 + 2\text{H}_2\text{SO}_4 + \text{I}_2 \\ \text{K}_2\text{S}_2\text{O}_8 + 2\text{HI} \longrightarrow \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{I}_2 \\ \text{Potassium peroxydisulphate} \end{array}$$

(vi) Precipitation reactions: HCl forms insoluble chlorides with the soluble salts of Ag, Pb and Hg(ous).

$$\begin{array}{c} \text{AgNO}_3 + \text{HCl} \longrightarrow \text{AgCl} + \text{HNO}_3 \\ \text{(White)} \\ \text{Pb(NO}_3)_2 + 2\text{HCl} \longrightarrow \text{PbCl}_2 + 2\text{HNO}_3 \\ \text{(White)} \\ \text{Hg}_2(\text{NO}_3)_2 + 2\text{HCl} \longrightarrow \text{Hg}_2\text{Cl}_2 + 2\text{HNO}_3 \\ \text{(White)} \end{array}$$

AgCl is insoluble in  $HNO_3$  but soluble in  $NH_4OH$ .  $PbCl_2$  is soluble in hot water while  $Hg_2Cl_2$  is soluble in aqua-regia.

HBr reacts with soluble salts of Ag and Pb.

$$AgNO_3 + HBr \longrightarrow AgBr + HNO_3$$
(Pale yellow)
$$Pb(NO_3)_2 + 2HBr \longrightarrow PbBr_2 + 2HNO_3$$
(White)

AgBr is insoluble in HNO<sub>3</sub> but sparingly soluble in NH<sub>4</sub>OH. PbBr<sub>2</sub> is soluble in hot water.

HI forms insoluble iodides with the salts of Ag, Pb and Hg (ic).

$$\begin{array}{c} \text{AgNO}_3 + \text{HI} & \longrightarrow \text{AgI} + \text{HNO}_3 \\ \text{(Yellow)} \end{array}$$
 
$$\text{Pb(CH}_3\text{COO)}_2 + 2\text{HI} & \longrightarrow \text{PbI}_2 + 2\text{CH}_3\text{COOH} \\ \text{(Yellow)} \end{array}$$
 
$$\text{HgCl}_2 + 2\text{HI} & \longrightarrow \text{HgI}_2 + 2\text{HCl} \\ \text{(Scarlet)} \end{array}$$

AgI is insoluble in HNO<sub>3</sub> and NH<sub>4</sub>OH. PbI<sub>2</sub> is soluble in hot water.

(vii) Action of halogens:  $F_2$  can displace  $Cl_2$ ,  $Br_2$  and  $I_2$  from HCl, HBr and HI.

$$\begin{aligned} & 2HCl + F_2 \longrightarrow 2HF + Cl_2 \\ & 2HBr + F_2 \longrightarrow 2HF + Br_2 \\ & 2HI + F_2 \longrightarrow 2HF + I_2 \end{aligned}$$

 $Cl_2$  can displace  $Br_2$  and  $I_2$  from HBr and HI and  $Br_2$  can displace only  $I_2$  from HI. Iodine can displace none.

(viii) Reaction with ammonia: HCl, HBr and HI combine with ammonia giving white fumes of ammonium halides.

Registration of the second

$$NH_3 + HCl \longrightarrow NH_4Cl$$
 (Ammonium chloride)  
 $NH_3 + HBr \longrightarrow NH_4Br$  (Ammonium bromide)  
 $NH_3 + HI \longrightarrow NH_4I$  (Ammonium iodide)

(ix) Acidic properties: All the three (HCl, HBr and HI) react with certain metals, their oxides, carbonates, hydroxides, etc., and form salts.

$$\begin{array}{c} \text{Mg} + 2\text{HX} \longrightarrow \text{Mg}\,\text{X}_2 + \text{H}_2 \\ \text{MgO} + 2\text{HX} \longrightarrow \text{Mg}\,\text{X}_2 + \text{H}_2\text{O} \\ \text{CaCO}_3 + 2\text{HX} \longrightarrow \text{CaX}_2 + \text{H}_2\text{O} + \text{CO}_2 \\ \text{NaHCO}_3 + \text{HX} \longrightarrow \text{NaX} + \text{H}_2\text{O} + \text{CO}_2 \\ \text{NaOH} + \text{HX} \longrightarrow \text{NaX} + \text{H}_2\text{O} \end{array}$$

[HX = HCl, HBr or HI]

(x) Action of salts: HCl, HBr or HI decompose the salts of weaker acids.

$$Na_{2}S + 2HX \longrightarrow 2NaX + H_{2}S$$

$$Ca_{3}P_{2} + 6HX \longrightarrow 3CaX_{2} + 2PH_{3}$$

$$Na_{2}SO_{3} + 2HX \longrightarrow 2NaX + H_{2}O + SO_{2}$$

$$2NaNO_{2} + 2HX \longrightarrow 2NaX + NO + NO_{2} + H_{2}O$$

$$Na_{2}S_{2}O_{3} + 2HX \longrightarrow 2NaX + SO_{2} + S + H_{2}O$$

## **Abnormal Properties of Hydrofluoric Acid**

Hydrofluoric acid differs from other halogen acids in the following respects:

- (i) Anhydrous hydrogen fluoride is a liquid at ordinary temperature while other halogen acids are gases. This is due to strong hydrogen bonding in hydrogen fluoride.
- (ii) It is very stable. It does not dissociate on heating while other halogen acids dissociate at definite temperatures.

It is due to decrease in the electronegativity and bond energy.

- (iii) It exists as associated molecule, H<sub>2</sub>F<sub>2</sub>, even in gaseous state. It forms two series of salts, *i.e.*, KHF<sub>2</sub>, K<sub>2</sub>F<sub>2</sub>. Other halogen acids have molecular formula, H X and form one series of salts.
  - HCl; Chlorides, e.g., NaCl, AgCl, FeCl<sub>3</sub>, BaCl<sub>2</sub>, etc.

HBr; Bromides, e.g., NaBr, AgBr, FeBr<sub>3</sub>, BaBr<sub>2</sub>, etc.

HI; Iodides, e.g., NaI, AgI, FeI3, BaI2, etc.

- (iv) It is a weak acid but is extremely stable. It is not oxidised by strong oxidising agents. On the other hand all other halogen acids are oxidised.
- (v) Hydrofluoric acid is highly poisonous and has a very high corrosive action on skin.
- (vi) Unlike other halogen acids, hydrofluoric acid attacks silica and glass. With silica, it forms silicon tetrafluoride and hydrofluosilicic acid.

$$SiO_2 + 2H_2F_2 \longrightarrow SiF_4 + 2H_2O$$
  
 $SiF_4 + H_2F_2 \longrightarrow H_2SiF_6$   
Hydrofluosilicic acid

Glass being a mixture of sodium and calcium silicates reacts with hydrofluoric acid forming sodium and calcium flurosilicates respectively.

$$Na_2SiO_3 + 3H_2F_2 \longrightarrow Na_2SiF_6 + 3H_2O$$
  
 $CaSiO_3 + 3H_2F_2 \longrightarrow CaSiF_6 + 3H_2O$ 

The etching of glass is based on these reactions.

(vii) When hydrofluoric acid is heated with a mixture of MnO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>, no gas is evolved. On the other hand, in case of HCl, HBr and HI acids, Cl<sub>2</sub> (yellowish green), Br<sub>2</sub> (reddish brown) and I<sub>2</sub> (violet) gases are evolved.

$$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + O$$
  
 $2HX + O \longrightarrow H_2O + X_2$ 

HX = HCl, HBr or HI

 $X_2 = \text{Cl}_2$ ,  $\text{Br}_2$  or  $\text{I}_2$ 

- (viii) With AgNO<sub>3</sub> solution, hydrofluoric acid gives no precipitate since AgF is formed which is soluble in water. On the other hand, HCl, HBr and HI give the precipitates of AgCl, AgBr and AgI respectively.
- (ix) Lead acetate does not form any precipitate with hydrofluoric acid while other halogen acids form precipitates of PbCl<sub>2</sub> (white), PbBr<sub>2</sub> (white) and PbI<sub>2</sub> (yellow) respectively.
- (x) With barium chloride solution,  $H_2F_2$  forms a white precipitate of  $BaF_2$  while other halogen acids do not form any precipitate since  $BaX_2$  (X = Br and I) are soluble.

$$H_2F_2 + BaCl_2 \longrightarrow BaF_2$$
 + 2HC

Same thing happens with the solutions of calcium chloride and strontium chloride as  $CaF_2$  and  $SrF_2$  are also insoluble.

## Uses of halogen acids

- (i) Hydrofluoric acid is used:
- (a) in the etching of glass.
- (b) in the manufacture of fluorine.
- (c) for removing silica from artificial graphite and other castings.
  - (d) as an antiseptic in brewing industries.
  - (e) for making fluorides. NaF is used as an insecticide.

AlF<sub>3</sub> is used in the extraction of aluminium. Fluorides of alkali metals and antimony are used as mordants in dyeing industry. UF<sub>6</sub> is used for separation of U<sup>235</sup> isotope by diffusion method.

#### (ii) Hydrochloric acid is used:

- (a) in the preparation of chlorine, chlorides and aqua-regia.
- (b) as a laboratory reagent.
- (c) for cleaning iron sheets during tin plating and galvanisation.
  - (d) for extraction of glue from animal tissues and bones.
  - (e) in medicines.

#### (iii) Hydrobromic acid is used:

- (a) as a laboratory reagent for preparing bromo derivatives of unsaturated organic compounds.
  - (b) for making NaBr and KBr which are used as sedatives.
  - (c) for making AgBr used in photography.

#### (iv) Hydroiodic acid is used:

- (a) as a reducing agent in organic chemistry.
- (b) for making KI which is used in medicines.
- (c) for making AgI which is used in photography.

COMPARISON	OF HALOGEN	ACIDE /HE	LICI	UDr and UIV
COMPANISON	OI HALOGEN	MUIDO (IIII)	1101,	noi anu mi

S.No.	Property	HF	HCl	HBr	Н
1.	Physical state at ordinary temperature	Liquid	Gas	Gas .	Gas
2.	Colour	Colourless	Colourless	Colourless	Colourless
3.	Smell	Choking	Choking	Irritating	Irritating
4.	Stability	Stable	Stable	Less stable than HCl	Much less stable
5.	Strength of the acid	A weak acid (Weakest)	Gaseous HCl is not acidic but aqueous solution is highly acidic	Greater than HCl	Strongest
6.	Reducing nature	No reducing nature	Acts as a reducing agent and is oxidised to Cl <sub>2</sub>	Stronger reducing agent than HCl and is oxidised to Br <sub>2</sub>	Strongest reducing agent of all the halogen acids
7	Action of MnO <sub>2</sub> and	No gas is evolved	-Chlorine-is-evolved	Bromine gas is evolved	Iodine (violet) vapours
~	H <sub>2</sub> SO <sub>4</sub>			Turns starch paper yellow	are evolved. Turns starch paper, violet
8.	Action with AgNO <sub>3</sub> solution	No precipitate	White precipitate, soluble in NH <sub>4</sub> OH	Pale yellow precipitate sparingly soluble in NH <sub>4</sub> OH	Yellow precipitate, insoluble in NH <sub>4</sub> OH
9.	Action of lead acetate	No precipitate	White precipitate dissolves	White precipitate dissolves	Yellow precipitate
	solution		in hot water	in hot water	dissolves in hot water
10.	Action of $X_2$	- American	Cl <sub>2</sub> is liberated only by F <sub>2</sub>	Br <sub>2</sub> is liberated by F <sub>2</sub> and Cl <sub>2</sub>	I <sub>2</sub> is liberated by F <sub>2</sub> , Cl <sub>2</sub> and Br <sub>2</sub>
11.	Confirmation test	With silica forms SiF <sub>4</sub> which on hydrolysis gives white deposit	Chromyl chloride	The aqueous solution on treatment with chlorine water in presence of	The aqueous solution or treatment with chlorine water in presence of
				chloroform gives brown colouration	chloroform gives violet colouration

## 12.8 OXIDES OF CHLORINE

Chlorine forms a number of oxides such as Cl<sub>2</sub>O, ClO<sub>2</sub>, Cl<sub>2</sub>O<sub>6</sub> and Cl<sub>2</sub>O<sub>7</sub>. All of them are unstable and highly reactive.

(i) Dichloro oxide, Cl<sub>2</sub>O: It is prepared by passing dry chlorine over freshly precipitated yellow mercuric oxide.

$$HgO + 2Cl_2(dry) \longrightarrow HgCl_2 + Cl_2O$$

It is a brownish yellow gas which condenses to an orange coloured liquid in a freezing mixture (b. pt. =  $2^{\circ}$ C). It has characteristic penetrating odour. Liquid Cl<sub>2</sub>O explodes readily on heating or sparking forming Cl<sub>2</sub> and O<sub>2</sub>. It also undergoes photochemical decomposition.

$$2Cl_2O \longrightarrow 2Cl_2 + O_2$$

It dissolves in water giving golden yellow solution of hypochlorous acid, HClO. It is thus anhydride of hypochlorous acid.

$$Cl_2O + H_2O \rightleftharpoons 2HClO$$

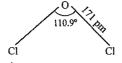
Its gaseous mixture with ammonia explodes violently.

$$3Cl_2O + 10NH_3 \longrightarrow 2N_2 + 6NH_4Cl + 3H_2O$$

It is a strong oxidising agent. It oxidises HCl to Cl<sub>2</sub>.

$$Cl_2O + 2HCl \longrightarrow 2Cl_2 + H_2O$$

 $Cl_2O$  has V-shaped structure. The oxygen atom undergoes  $sp^3$  hybridization. The Cl—O—Cl bond angle is 110.9°.



(ii) Chlorine dioxide, ClO<sub>2</sub>: Pure ClO<sub>2</sub> is obtained by passing dry Cl<sub>2</sub> over AgClO<sub>3</sub> heated to 90°C.

$$2AgClO_3 + Cl_2(dry) \longrightarrow 2AgCl + 2ClO_2 + O_2$$

It can also be obtained by the action of Cl<sub>2</sub> on sodium chlorite.

$$2NaClO_2 + Cl_2 \longrightarrow 2NaCl + 2ClO_2$$

It can be condensed by cooling to a coloured liquid (b.pt.  $11^{\circ}$ C). The gas explodes and is decomposed to  $Cl_2$  and  $O_2$  by an electric spark. It dissolves in water giving a mixture of chlorous acid and chloric acid.

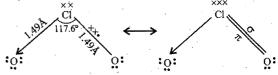
$$2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$$

With alkalies, it gives a mixture of chlorite and chlorate.

$$2ClO_2 + 2KOH \longrightarrow KClO_2 + KClO_3 + H_2O$$

It is a powerful oxidising and bleaching agent.

It has an angular structure with O—Cl—O bond angle of 117.6°C. The molecule is supposed to contain a three electron bond. Its structure is believed to be a resonance hybrid of the following two structures:



The structure arises from  $sp^3d$  hybridization of Cl-atom. The molecule is paramagnetic due to the presence of three electron bond.

(iii) Dichlorine hexoxide,  $Cl_2O_6$ : It is obtained by mixing chlorine dioxide with ozonised air at  $0^{\circ}$ C.

$$2ClO_2 + 2O_3 \longrightarrow Cl_2O_6 + 2O_2$$

It is a dark red liquid. It is unstable and decomposed into ClO<sub>2</sub> and O<sub>2</sub>. It is a strong oxidising agent. It reacts with water forming chloric and perchloric acids.

$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$

It reacts with alkalies to give chlorates and perchlorates.

$$Cl_2O_6 + 2KOH \longrightarrow KClO_3 + KClO_4 + H_2O$$

With HF, it gives HClO<sub>4</sub> and chloryl fluoride.

$$Cl_2O_6 + HF \longrightarrow HClO_4 + ClO_2F$$

In the vapour state it exists as ClO<sub>3</sub> molecule which has odd number of electrons and hence paramagnetic while in liquid state it is in dimeric form having even number of electrons and hence diamagnetic in nature.

$$2ClO_3 \rightleftharpoons Cl_2O_6$$

The exact structure is unknown. However, the following structure containing Cl—Cl linkage is proposed in which each chlorine is  $sp^3$  hybridized.

The molecule is diamagnetic and has no unpaired electron. (iv) Chlorine heptoxide,  $Cl_2O_7$ : It is formed by dehydration of perchloric acid with  $P_2O_5$  at  $-10^{\circ}C$ .

$$2HClO_4 \xrightarrow{P_2O_5} Cl_2O_7 + H_2O$$

It is a colourless oily liquid which is explosive in nature. It slowly reacts with water forming perchloric acid. It is, thus, anhydride of perchloric acid.

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

It is less reactive in comparison to lower oxides of chlorine.  $Cl_2O_7$  has the structure  $O_3Cl-O-ClO_3$  in which two tetrahedral are sharing one O-atom.

## 12.9 OXY-ACIDS OF CHLORINE

## 🛮 (A) Hypochlorous Acid, HClO

The acid is known only in solution. It is obtained by shaking precipitated HgO with chlorine water.

$$2$$
HgO +  $2$ Cl<sub>2</sub> +  $H_2$ O  $\longrightarrow$  Hg<sub>2</sub>OCl<sub>2</sub> +  $2$ HClO Oxychloride of mercury

Commercially, it is obtained by passing CO<sub>2</sub> through suspension of bleaching powder and then distilling.

$$2CaOCl_2 + H_2O + CO_2 \longrightarrow CaCl_2 + CaCO_3 + 2HClO$$

It is a weak acid. Its concentrated solution is yellow in colour while dilute solution is colourless. It is unstable and decomposes.

$$2HClO \longrightarrow 2HCl + O_2$$

It dissolves magnesium with evolution of hydrogen.

$$Mg + 2HClO \longrightarrow Mg(ClO)_2 + H_2$$

With alkalies, it forms salts called hypochlorites.

It acts as a powerful oxidising and bleaching agent. This is due to release of nascent oxygen easily.

$$HClO \longrightarrow HCl + O$$

CIO ion has linear shape. Linear shape results from sp<sup>3</sup> hybridization of Cl-atom.



## Bleaching powder, CaOCl<sub>2</sub>·H<sub>2</sub>O

Bleaching powder is also called calcium chlorohypochlorite because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid. It is represented as:

It is manufactured by the action of chlorine on dry slaked lime, Ca(OH)<sub>2</sub>, at 40°C.

$$Ca(OH)_2 + Cl_2 \longrightarrow Ca(OCl)Cl + H_2O$$

This is the Odling view about its formation. There is another view proposed by Clifford according to which bleaching powder is a mixture of calcium hypochlorite and basic calcium chloride.

$$\begin{array}{c} 2 \text{Ca}(\text{OH})_2 + 2 \text{Cl}_2 \longrightarrow \text{Ca}(\text{OCl})_2 + \text{CaCl}_2 + 2 \text{H}_2 \text{O} \\ \hline \text{CaCl}_2 + \text{Ca}(\text{OH})_2 + \text{H}_2 \text{O} \longrightarrow \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \text{H}_2 \text{O} \\ \hline 2 \text{Cl}_2 + 3 \text{Ca}(\text{OH})_2 \longrightarrow \text{Ca}(\text{OCl})_2 + \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \text{H}_2 \text{O} + \text{H}_2 \text{O} \\ \hline \text{Bleaching powder} \end{array}$$

The manufacture of bleaching powder is carried out in any one of the following plants:

- (i) Hasenclever's plant (Old process),
- (ii) Beckmann's plant (Modern process).
- (i) Hasenclever's plant: It consists of a number of cast-iron horizontal cylinders, each provided with a rotating shaft fitted with blades and arranged as shown in Fig. 12.10.

The dry slaked lime is introduced through the hopper in the uppermost cylinder. It is pushed onwards with the help of the blades when the shaft rotates. A stream of chlorine is

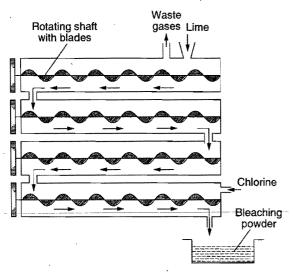
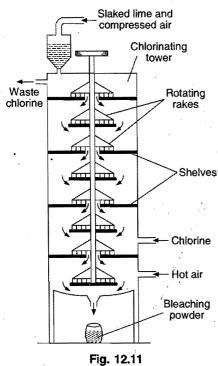


Fig. 12.10

admitted from the bottom and passes upwards. The chlorine is completely absorbed by the time till it reaches the top cylinder. Bleaching powder is collected in a barrel placed below an outlet in the lowermost cylinder while the waste gases escape from the top.

(ii) Beckmann's plant (Modern process): It consists of a vertical cast-iron tower. The tower is provided with a hopper at the top, two inlets near the base (one for chlorine and other for hot air) and an exit for waste gases near the top (Fig. 12.11).



The tower is fitted with eight shelves at different heights each equipped with rotating rakes. The slaked lime is introduced through the hopper and it comes in contact with chlorine which slowly moves upwards. Bleaching powder is collected in a barrel at the base.

The chlorine used in the manufacture of bleaching powder should be dilute and the temperature should be maintained below 40°C.

## **Properties**

- (a) It is a pale yellow powder. It has a strong smell of chlorine. It is soluble in water but a clear solution is never formed due to the presence of impurities.
- (b) On long standing, it undergoes auto-oxidation into calcium chlorate and calcium chloride.

$$6CaOCl_2 \longrightarrow Ca(ClO_3)_2 + 5CaCl_2$$

(c) In presence of cobalt chloride, CoCl<sub>2</sub>, it loses its oxygen.

$$2CaOCl_2 \xrightarrow{CoCl_2} 2CaCl_2 + O_2$$

(d) In presence of a slight amount of a dilute acid, it loses oxygen.

$$2CaOCl_2 + H_2SO_4 \longrightarrow CaCl_2 + CaSO_4 + 2HClO \longrightarrow HClO \longrightarrow HCl + O$$

On account of the formation of nascent oxygen, it shows oxidising and bleaching properties.

#### (i) Oxidising properties:

$$\begin{array}{c} \text{CaOCl}_2 + \text{H}_2\text{S} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{S} \\ \text{CaOCl}_2 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{CaCl}_2 + \text{H}_2\text{O} \\ \text{CaOCl}_2 + \text{KNO}_2 \longrightarrow \text{CaCl}_2 + \text{KNO}_3 \\ 3\text{CaOCl}_2 + 2\text{NH}_3 \longrightarrow 3\text{CaCl}_2 + 3\text{H}_2\text{O} + \text{N}_2 \\ \text{CaOCl}_2 + 2\text{KI} + 2\text{HCl} \longrightarrow \text{CaCl}_2 + 2\text{KCl} + \text{H}_2\text{O} + \text{I}_2 \\ \text{Na}_3\text{AsO}_3 + \text{CaOCl}_2 \longrightarrow \text{CaCl}_2 + \text{Na}_3\text{AsO}_4 \end{array}$$

#### (ii) Bleaching action:

Coloured matter + [O] ----- Colourless product

(e) It loses its chlorine by the action of dilute acids (in excess) or carbon dioxide.

$$CaOCl2 + 2HCl \longrightarrow CaCl2 + H2O + Cl2$$

$$CaOCl2 + H2SO4 \longrightarrow CaSO4 + H2O + Cl2$$

$$CaOCl2 + CO2 \longrightarrow CaCO3 + Cl2$$

The amount of chlorine obtained from a sample of bleaching powder by treatment with excess of dilute acids or carbon dioxide is called available chlorine. A good sample of bleaching powder contains 35–38% of available chlorine.

(f) Bleaching powder converts acetone or ethyl alcohol into chloroform.

$$\begin{array}{c|c} \text{CaOCl}_2 + \text{H}_2\text{O} & \longrightarrow \text{Ca}(\text{OH})_2 + \text{Cl}_2 \\ \text{CH}_3 & & \text{CCl}_3 \\ \text{CH}_3 & & \text{CH}_3 \\ \text{CCl}_3 & & \text{CH}_3\text{COO} \\ \text{CH}_3 & & \text{CH}_3\text{COO} \\ \text{CH}_3 & & \text{Chloroform} \\ \end{array}$$

### Uses of Bleaching Powder

It is used (i) as a disinfectant and germicide especially in the sterilisation of drinking water. (ii) for manufacture of chloroform. (iii) for making wool unshrinkable. (iv) as an oxidising agent in industry. (v) mainly as bleaching agent for cotton, linen and wood pulp. However, delicate articles like straw, silk, ivory, etc., are not bleached by bleaching powder.

#### Estimation of available chlorine

The maximum percentage of available chlorine as calculated from Odling's formula comes to 49%.

The estimation of available chlorine in a given sample of bleaching powder is done volumetrically by

(i) Iodometric method or (ii) Arsenite method.

**Iodometric method:** A weighed quantity of bleaching powder is suspended in water and treated with excess of acetic acid and potassium iodide. The liberated iodine is estimated by treating with a standard solution of sodium thiosulphate using starch as an indicator.

$$\begin{array}{c} \text{CaOCl}_2 + 2\text{CH}_3\text{COOH} \longrightarrow (\text{CH}_3\text{COO})_2\text{Ca} + \text{Cl}_2 + \text{H}_2\text{O} \\ 2\text{KI} + \text{Cl}_2 \longrightarrow 2\text{KCl} + \text{I}_2 \\ 2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6 \end{array}$$

Let V mL of  $\frac{N}{r}$  Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> be used for W g of a sample of bleaching powder.

$$V \text{ mL } \frac{N}{x} \text{Na}_2 \text{S}_2 \text{O}_3 \Longrightarrow V \text{ mL } \frac{N}{x} \text{ Iodine}$$

$$= V \text{ mL } \frac{N}{x} \text{ Chlorine}$$

$$= \frac{35.5}{x} \times \frac{V}{1000} \text{ g Chlorine}$$
Thus, % of available chlorine

$$=\frac{35.5\times V\times 100}{x\times 1000\times W}\ =\ \frac{3.55\times V}{x\times W}$$

The percentage of available chlorine in the commercial samples of bleaching powder is usually between 33-38%. The low value is due to the following factors:

- (i) Incomplete reaction between slaked lime and chlorine during its formation.
- (ii) Impurities present in the original slaked lime used for the manufacture.
  - (iii) Decomposition of bleaching powder when kept in air.

## **(B) Chlorous Acid, HCIO<sub>2</sub>**

It is obtained in aqueous solution when barium chlorite suspension in water is treated with H<sub>2</sub>SO<sub>4</sub>. The insoluble barium sulphate is filtered off.

$$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_2$$

The freshly prepared solution is colourless but it soon decomposes to ClO<sub>2</sub> which makes the solution yellow.

$$5HClO_2 \longrightarrow 4ClO_2 + HCl + 2H_2O$$

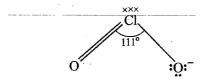
The acid undergoes auto-oxidation.

$$2HClO_2 \longrightarrow HClO + HClO_3$$

The acid liberates iodine from KI.

$$4KI + HClO_2 + 2H_2O \longrightarrow 4KOH + HCl + 2I_2$$

Chlorite ion, ClO<sub>2</sub>, has angular shape. This shape is due to sp<sup>3</sup> hybridization of Cl-atom.



## (C) Chloric Acid, HCIO<sub>3</sub>

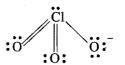
This acid is only known in solution. The acid is prepared by the action of dilute H<sub>2</sub>SO<sub>4</sub> on barium chlorate.

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_3$$

BaSO<sub>4</sub> is filtered off.

Concentrated acid is colourless and pungent smelling liquid. It decomposes in light. However, it is stable in dark. It acts as a strong oxidising and bleaching agent in light. Organic substances like paper, cotton, wool, etc., catch fire in contact with the acid.

Chlorate ion, ClO<sub>3</sub>, has pyramidal shape. The shape results due to  $sp^3$  hybridization of Cl-atom.



## (D) Potassium Chlorate, KClO<sub>3</sub>

Potassium chlorate is the salt of chloric acid, HClO<sub>3</sub>. HClO<sub>3</sub> is known only in solution but its salts are quite stable in free state under ordinary conditions.

Potassium chlorate is formed in laboratory by passing chlorine gas through hot and concentrated solution of potassium hydroxide.

$$6KOH + 3Cl_2 \longrightarrow 5KCl + KClO_3 + 3H_2O$$

When the solution is cooled, crystals of KClO<sub>3</sub> are obtained.

#### Manufacture

(i) Old process: This process involves chlorination of lime with the formation of calcium chlorate.

$$6Ca(OH)_2 + 6Cl_2 \longrightarrow Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O$$

#### (x) Structures:

Molecule	Bond pairs	Lone pairs	Total number of electron pairs around 'A'	Hybridized state of central atom 'A'	Geometry and actual shape
AB (CIF, BrF, BrCl, ICl, IBr)	1	. 3	. 4	$sp^3$	Tetrahedral (Linear)
					В
•			•		
AB <sub>3</sub> (ClF <sub>3</sub> , BrF <sub>3</sub> , ICl <sub>3</sub> )	. 3	2	5	sp <sup>3</sup> d	Trigonal bipyramid (T-shaped) B
		s e e e e e e e e e e e e e e e e e e e			A
$AB_5$ (BrF <sub>5</sub> , IF <sub>5</sub> )	5	1	6	$sp^3d^2$	Octahedral (Square pyramidal)
					B
<i>AB</i> <sub>7</sub> (IF <sub>7</sub> )	7	0	7.	$sp^3d^3$	Pentagonal bipyramidal
					B B B

## 12.11 POLYHALIDES

Halide ions often react with molecules of halogens or interhalogen and form polyhalide ions. Iodine is only slightly soluble in water. Its solubility is greatly increased if some iodide ions are present in the solution. The increase in solubility is due to formation of a polyhalide ion,  $I_3^-$ .

$$I^- + I_2 \longrightarrow I_3^-$$

This ion is stable in aqueous solution and in ionic crystals. More complex ions such as  $I_5^-$ ,  $I_7^-$  and  $I_9^-$  have also been prepared. The  $Br_3^-$  and  $Cl_3^-$  ions are much less stable than  $I_3^-$ .

Many polyhalides are known which contain two or three different halogens, for example K[ICl<sub>2</sub>], K[ICl<sub>4</sub>], Cs[IBrF] and K[IBrCl]. These are formed from interhalogens and metal halides.

$$ICl + KCl \longrightarrow K[ICl_2]$$

$$ICl_3 + KCl \longrightarrow K[ICl_4]$$

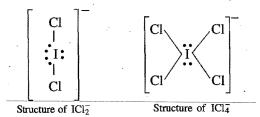
$$ICl + KBr \longrightarrow K[IBrCl]$$

Polyhalides are typical ionic compounds (crystalline, stable and soluble in water, conduct electricity when in solution) though they tend to decompose on heating. The products of decomposition are governed by the lattice energy of the products. The lattice energy of the alkali metal halides is higher for the smaller halide ions, so the smaller halogen remain bonded to the metal.

$$\begin{array}{ccc} Rb[ICl_2] & \xrightarrow{Heat} & RbCl + ICl \\ K[BrICl] & \xrightarrow{Heat} & KCl + IBr \\ Cs[I_3] & \longrightarrow & CsI + I_2 \end{array}$$

All polyhalides are coloured. The bromo iodides are red and chlorobromides are yellow, *i.e.*, the depth of the colour increases

with increase of atomic number of the halogen atoms present. Trihalide anions like  $ICl_2$ ,  $I_3$ , [IBrCl] have symmetrical linear shape. This shape results from  $sp^3d$  hybridization of central atom. Similarly the structures of the pentahalide ions  $[ICl_4]$  and  $[BrF_4]$  are square planar. This shape results from  $sp^3d^2$  hybridization of central atom.



## 12.12 BASIC PROPERTIES OF IODINE

In general, metallic or basic properties in halogens increase on moving down the group. Iodine shows maximum basic properties in halogen family elements although it is not a metal. The compounds in which iodine functions as cationic constituent are numerous and well established. Some examples are given below:

Compounds containing unipositive iodine (I<sup>+</sup>)

ICl, IBr, INO<sub>3</sub>,  $[I(py)_2]NO_3$ ,  $[I(py)_2]ClO_4$ ,  $I_2SO_4$ 

Compounds containing tripositive iodine (I<sup>3+</sup>)

 $I(ClO_4)_3,\ I(CH_3COO)_3,\ IPO_4,\ I(NO_3)_3,\ ICl_3$ 

# 12.13 PSEUDOHALIDES AND PSEUDOHALOGENS

A few ions are known, consisting of two or more electronegative atoms of which at least one is nitrogen, that have properties similar to those of halide ions. These ions are called pseudohalide ions. Pseudohalide ions are univalent and these form salts resembling halide salts. For example, sodium salts are soluble in water but the silver salts are insoluble. The hydrogen compounds are acids like the halogen acids, HX. The pseudohalide ions are:

Cyanide ion (CN) ; Isocyanide ion (NC)

Cyanate ion (OCN) ; Fulminate ion (ONC)

Thiocyanate ion (SCN) ; Isothiocyanate ion (NCS)

Selenocyanate ion (SeCN) ; Tellurocyanate ion (TeCN)

Azide ion (N3) ; Azido carbon disulphide ion (SCSN3)

The salts formed by above ions are called pseudohalides. As the dimers of halide ions are called halogens, the covalent dimers of the pseudohalide ions are called pseudohalogens or halogenoids. So far only few of pseudohalogens have been isolated and characterised. The pseudohalogens known are:

Cyanogen (CN)<sub>2</sub> ; Oxycyanogen (OCN)<sub>2</sub> Thiocyanogen (SCN)<sub>2</sub> ; Selenocyanogen (SeCN)<sub>2</sub> Tellurocyanogen (TeCN)<sub>2</sub> ; Azido carbon disulphide (SCSN<sub>3</sub>)<sub>2</sub>

The best known pseudohalide is CN. This resembles Cl, Br and I in the following respects:

- (i) It forms an acid, HCN.
- (ii) It can be oxidised to (CN)<sub>2</sub> molecule.
- (iii) It forms insoluble salts with Ag<sup>+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup>.
- (iv) It forms large number of complexes similar to halide complexes, e.g.,

 $\left[Cu(CN)_4\right]^{2-}$  and  $\left[CuCl_4\right]^{2-}$ ,  $\left[Co(CN)_6\right]^{3-}$  and  $\left[CoCl_6\right]^{3-}$ 

- (v) Inter-pseudohalogen compounds ClCN, BrCN and ICN can be formed.
- (vi) AgCN is insoluble in water but soluble in ammonia like AgCl.

(vii) HCN is oxidised like HCl.

$$MnO_2 + 4HCN \longrightarrow Mn(CN)_2 + (CN)_2 + 2H_2O$$
  
 $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$ 

# SOME SOLVED PROBLEMS

**Example 1.** Which of the halogens (F, Cl, Br or I) provides an example of?

- (a) the weakest acid, HX,
- (b) the largest atom,
- (c) the smallest ionisation potential,
- (d) the strongest oxidising agent,
- (e) the highest electron affinity,
- (f) the highest electronegativity,
- (g) liquid state under ordinary conditions.

#### **Solution:**

- (a) The weakest acid is HF. Thus, fluorine forms the weakest acid.
  - (b) The largest atom is of iodine.

- (c) The smallest ionisation potential is of iodine.
- (d) The strongest oxidising agent is fluorine.
- (e) The highest electron affinity is of chlorine.
- (f) Fluorine has the highest electronegativity.
- (g) Bromine is in liquid state under ordinary conditions.

**Example 2.** Arrange the halogen hydrides in the increasing order of:

(i) dipole moment, (ii) reducing power, (iii) thermal stability, (iv) bond length, (v) ionic character.

#### **Solution:**

- (i) HI < HBr < HCl < HF (Increasing dipole moment)
- (ii) HF < HCl < HBr < HI (Increasing reducing nature)
- (iii) HI < HBr < HCl < HF (Increasing thermal stability)

- (iv) HF < HCl < HBr < HI (Increasing bond length)
- (v) HI < HBr < HCl < HF (Increasing ionic character)

**Example 3.** Give relevant chemical equations for the preparation of:

- (i) Chlorine from sodium chloride.
- (ii) Iodine from Kelp.
- (iii) Hydrobromic acid from potassium bromide.
- (iv) Bleaching powder from slaked lime.
- (v) KClO<sub>3</sub> from sodium chloride.

#### **Solution:**

(i) Chlorine is obtained from sodium chloride by carrying the electrolysis of its aqueous solution.

NaCl 
$$\rightleftharpoons$$
 Na<sup>+</sup> + Cl

H<sub>2</sub>O  $\rightleftharpoons$  H<sup>+</sup> + OH

At Cathode: H<sup>+</sup> + e<sup>-</sup>  $\longrightarrow$  H

2H  $\longrightarrow$  H<sub>2</sub>↑

At Anode: Cl<sup>-</sup>  $\rightleftharpoons$  Cl+ e<sup>-</sup>

2Cl  $\longrightarrow$  Cl<sub>2</sub>↑

(ii) The ash of sea-weeds (Kelp) is extracted with water, the sulphates and chlorides of Na and K present in it are removed by crystallisation. The mother liquor is now heated with  $MnO_2$  and conc.  $H_2SO_4$ . The iodine vapours are collected in earthen jars.

$$2\text{NaI} + 3\text{H}_2\text{SO}_4 + \text{MnO}_2 \longrightarrow 2\text{NaHSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{I}_2$$

(iii) HBr is prepared by heating KBr with conc. phosphoric acid.

$$3KBr + H_3PO_4 \longrightarrow K_3PO_4 + 3HBr$$

(iv) Slaked lime is treated with chlorine gas by slowly moving forward dry slaked lime in a series of shelves provided with rotating rakes.

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 \cdot H_2O$$

(v) Sodium chlorate is first obtained by carrying electrolysis of hot concentrated solution of sodium chloride in an electrolytic cell.

NaCl 
$$\xrightarrow{\text{Electrolysis}}$$
  $H_2 + Cl_2$  Solution  $Cathode$  Anode

$$Na^+ + OH^- \longrightarrow NaOH$$

Cl<sub>2</sub> reacts with NaOH forming NaClO<sub>3</sub>.

$$6$$
NaOH +  $3$ Cl<sub>2</sub>  $\longrightarrow$   $5$ NaCl + NaClO<sub>3</sub> +  $3$ H<sub>2</sub>O

KCl is added to form sparingly soluble KClO<sub>3</sub>.

$$NaClO_3 + KCl \longrightarrow KClO_3 + NaCl$$

Example 4. A liquid A is treated with Na<sub>2</sub>CO<sub>3</sub> solution. A mixture of two salts B and C are produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid A again. Identify A, B and C and write the equations involved.

[LLT. 1997]

#### **Solution:**

The liquid A is bromine which on treatment with sodium carbonate forms a mixture of NaBr and NaBrO<sub>3</sub> (sodium

bromate). The mixture with conc.  $H_2SO_4$  on distillation gives the liquid bromine again.

$$3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$$
  
 $5NaBr + NaBrO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 3Br_2 + 3H_2O_3$ 

**Example 5.** Gradual addition of KI solution to  $Bi(NO_3)_3$  solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions. [I.I.T. 1996]

#### Solution:

Bi(NO<sub>3</sub>)<sub>3</sub> undergoes hydrolysis. Nitric acid is formed. HNO<sub>3</sub> oxidises KI, *i.e.*, I<sub>2</sub> (brown ppt.) is formed. The precipitated iodine dissolves in excess of KI and forms a yellow coloured solution of KI<sub>3</sub>.

$$\begin{array}{c} \text{Bi(NO}_3)_3 \, + \, \text{H}_2\text{O} \longrightarrow \text{Bi(OH)(NO}_3)_2 \, + \, \text{HNO}_3 \\ \\ 6\text{KI} \, + \, 8\text{HNO}_3 \longrightarrow \, 6\text{KNO}_3 \, + \, 2\text{NO} \, + \, 3\text{I}_2 \, + \, 4\text{H}_2\text{O} \\ \\ \text{Brown ppt.} \\ \\ \text{KI} \, + \, \text{I}_2 \longrightarrow \, \text{KI}_3 \\ \\ \text{Yellow soln.} \end{array}$$

**Example 6.** An inorganic compound (X) gives a brick red flame on performing flame test. This compound gives the following tests also.

- (a) Smells of chlorine when placed in moist air.
- (b) If KI and CH<sub>3</sub>COOH are added to the suspension in water, a brown colour is obtained.

Identify (X) and write down equations for reactions at steps (a) and (b).

#### **Solution:**

Compound (X) gives a brick red flame in flame test. Thus, it is a calcium compound. It smells of chlorine on exposure suggests that it is bleaching powder. It is confirmed by reaction (b).

(a) 
$$6\text{CaOCl}_2 \longrightarrow 5\text{CaCl}_2 + \text{Ca}(\text{ClO}_3)_2$$
  
 $\text{CaOCl}_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{Cl}_2$   
(b)  $\text{CaOCl}_2 + 2\text{CH}_3\text{COOH} \longrightarrow (\text{CH}_3\text{COO})_2\text{Ca} + \text{H}_2\text{O} + \text{Cl}_2$   
 $2\text{KI} + \text{Cl}_2 \longrightarrow 2\text{KCl} + \text{I}_2$ 

**Example 7.** Explain the following:

- (i) In the preparation of HI from KI, phosphoric acid is preferred to sulphuric acid.
  - (ii) Boiling point of HCl is lower than HF. [M.L.N.R. 1992]
- (iii) F—F bond in fluorine is weaker than Cl—Cl bond in chlorine. [M.L.N.R. 1993]
- (iv) Fluorine exhibits only oxidation state -1 while other halogens exhibit negative as well as positive oxidation states.
- (v) Bleaching powder loses its bleaching property when kept in an open bottle for a long time.

#### **Solution:**

(i) Besides acidic nature of sulphuric acid, it acts as an oxidising agent. H<sub>2</sub>SO<sub>4</sub> oxidises HI (reducing agent) formed from KI into iodine. Thus, H<sub>3</sub>PO<sub>4</sub> is preferred as it does not oxidise HI.

$$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$
  
 $H_2SO_4 + 2HI \longrightarrow I_2 + SO_2 + 2H_2O$ 

- (ii) In HF, there is hydrogen bonding. It is, therefore, an associated liquid. No hydrogen bonding is present in HCl. Only van der Waals' forces are present. This is the reason why boiling point of HCl is lower than HF.
- (iii) The dissociation energy of F—F bond is lower than Cl—Cl bond.

The low dissociation energy of fluorine is due to high interelectronic repulsions between non-bonding electrons in the 2porbitals as the size of fluorine atom is small. As a result F—F bond is weaker than Cl—Cl bond.

- (iv) Fluorine is the most electronegative element. It shows only -1 oxidation state as it saturates its valency shell. It cannot show any positive oxidation state as d-orbitals are not present in valency shell while d-orbitals are present in rest of the halogens.
- (v) Bleaching action of bleaching powder is due to release of Cl<sub>2</sub> at the time of application. Chlorine is lost by bleaching powder on long standing in open by the following two processes.

(a) 
$$CaOCl_2 + CO_2(air) \longrightarrow CaCO_3 + Cl_2$$

(b) 
$$6\text{CaOCl}_2 \longrightarrow 5\text{CaCl}_2 + \text{Ca(ClO}_3)_2$$

Thus, CaCl<sub>2</sub> and Ca(ClO<sub>3</sub>)<sub>2</sub> do not release Cl<sub>2</sub> at the time of use. Hence, bleaching property is lost by bleaching powder on exposure for long time.

**Example 8.** Fluorine does not form oxy-acids but other halogens do, why?

#### **Solution:**

In oxy-acids, the central element always exhibits positive oxidation states. Fluorine, being the most electronegative, never shows positive oxidation states, hence F does not form oxy-acids.

Other halogens have the tendency to show positive oxidation states and hence form oxy-acids.

**Example 9.** (a) Explain why ClF<sub>3</sub> exists whereas FCl<sub>3</sub> does not?

(b) Both NO and ClO<sub>2</sub> are odd electron species. NO dimerises but ClO<sub>2</sub> does not. Why?

#### Solution:

(a)  $CIF_3$  is known because chlorine can exhibit +3 oxidation state due to promotion of 3p-electron to 3d vacant orbital.

3s 3p	3d	
$\uparrow\downarrow$ $\uparrow\downarrow\uparrow\downarrow$ $\uparrow$		Ground state chlorine atom
$\uparrow \downarrow \qquad \uparrow \qquad \uparrow$	<u> </u>	Excited state
sp <sup>3</sup> d-hybridization	on	

Each of the three singly occupied orbitals overlap with *p*-orbital of each of the three fluorine atoms to form ClF<sub>3</sub> (trigonal bipyramidal geometry, T-shaped molecule).

No d-orbitals are present in the valency shell of fluorine and thus excitation is not possible. Fluorine, therefore, does not exhibit positive oxidation state and so the formation of FCl<sub>3</sub> is not possible.

(b) In NO, the size of nitrogen atom is small and the odd electron is attracted by only one oxygen atom while in ClO<sub>2</sub>, the size of chlorine atom is comparatively large and odd electron is attracted by two oxygen atoms. As a result, the odd electron on N in NO is localised while the odd electron on chlorine in ClO<sub>2</sub> is delocalised. Thus, NO has a tendency to dimerise but-ClO<sub>2</sub> does not.

**Example 10.** Assign appropriate reasons for each of the following statements.

- (a) More metal fluorides are ionic in nature than metal chlorides.
- (b) Addition of  $Cl_2$  to KI solution gives it a brown colour but excess of  $Cl_2$  turns it colourless.
  - (c) Perchloric acid is a stronger acid than sulphuric acid.
- (d) Fluorine does not undergo disproportionation reactions but other halogens do.

#### **Solution:**

- (a) A bigger anion is more easily polarized than a smaller anion by the same metal cation according to Fajan's rules. F ion is smaller in size in comparison to Cl ion. Thus, the metal fluoride is more ionic than the metal chloride for the same metal cation.
- (b) Chlorine being more stronger oxidising agent than I<sub>2</sub>, displaces iodine from KI which brings brown colour to the solution. In excess of Cl<sub>2</sub>, the liberated iodine is further oxidised to iodic acid and solution becomes colourless.

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$
(Brown)
$$I_2 + 5Cl_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$$
(Colourless)

- (c) The oxidation state of chlorine in  $HClO_4$  is +7 while that of S in  $H_2SO_4$  is +6. Thus O—H group in  $HClO_4$  is easily broken than in  $H_2SO_4$ . Hence,  $HClO_4$  is a stronger acid in comparison to  $H_2SO_4$ .
- (d) F being the most electronegative element shows only -1 oxidation state while other halogens show both negative (-1) and positive (+1, +3, +5, +7) oxidation states. Thus, fluorine does not show disproportionation reactions.

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# **SUMMARY AND IMPORTANT POINTS TO REMEMBER**



- 1. 17th or VIIA group of the periodic table consists of fluorine, chlorine, bromine, iodine and astatine. These elements are collectively called as **halogens** as their salts are found in sea water (Halogen is a Greek word meaning sea salt).
- 2. Halogens are p-block elements as the last differentiating electron is accommodated on np subshell. These elements have seven electrons in their outermost shell, i.e., they have  $ns^2np^5$  configuration.

ns			np		
 $\uparrow\downarrow$	-	$\uparrow\downarrow$	_↑↓	1	_

They are all paramagnetic atoms.

- 3. These are highly reactive elements and never found free in nature but always in combined state. The salts of chlorine, bromine and iodine are found in sea water. The most common compounds of chlorine found on earth surface are common salt or table salt or rock salt (NaCl), sylvine (KCl), horn salt (AgCl), carnallite (MgCl<sub>2</sub>·KCl·6H<sub>2</sub>O), etc. Ashes of certain deep sea-weeds (Laminaria species) contain 0.5% of iodine as iodides. Chile saltpetre (caliche) contains NaIO<sub>3</sub> in minute quantity (0.2%). Bromine is usually obtained from sea water. The last member, astatine, is radioactive in nature.
- **4.** All halogens exist as diatomic molecules  $(X_2)$ . At room temperature,  $Cl_2$  and  $F_2$  are gases,  $Br_2$  is a fuming liquid while  $I_2$  is a volatile solid. The intermolecular forces are weak van der Waals' forces, whose magnitude increases from  $F_2$  to  $I_2$ . The melting/boiling points of halogens increase down the group.
- 5. Atomic radii are smallest within their respective periods. The atomic radii increase from F to I in moving down the group. They readily form  $X^-$  ions and the ionic radii also increase from  $F^-$  to  $I^-$ .
- 6. These elements have high ionisation energies. The values decrease in moving down the group. Iodine forms positive ions, i.e., it shows metallic nature. In the group, non-metallic decreases from F to I.
- 7. All the halogens are coloured.

The colour of the halogens is due to absorption of some wavelengths of visible light by their molecules to cause the promotion of electrons to higher energy molecular orbitals.

8. (a) The halogens have high electronegativity values. The values decrease from F to I.

- (b) The values of atomic volume and density increase steadily from F to I.
- (c) Halogens have high values of electron affinities.

The low value of electron affinity of fluorine is probably due to small size of fluorine atom, *i.e.*, electron density is high which hinders the addition of an extra electron.

Bond length (X—X) increases from F to I.
 Bond energy of F<sub>2</sub> molecule is, however, low inspite of shorter bond length.

Lower value of bond dissociation energy of fluorine is due to high interelectronic repulsions between non-bonding electrons in 2p-orbitals of fluorine.

- 10. (a) All halogens show a common oxidation state of -1 since each halogen having seven electrons in the valency shell tries to accept one more electron to attain 8 electrons when combines with less electronegative element.
  - (b) Fluorine being most electronegative, always shows −1 oxidation state only.
  - (c) Chlorine, bromine and iodine show positive oxidation states +1, +3, +5 and +7, +3, +5 and +7 oxidation states due to the promotion of valency electrons to *d*-orbitals which are vacant.
  - (d) Besides +3, +5 and +7 oxidation states, +4 and +6 oxidation states are also shown by these elements in oxides and oxyacids.
- 11. Standard reduction potentials of halogens are positive and decrease from F to I. Thus, halogens act as strong oxidising agents and their oxidising power decreases from F to I. In general, a halogen of low atomic number will oxidise the halide ion of higher atomic number.
- 12. F ion does not show any reducing nature but Cl, B and I ion act as reducing agents and their reducing nature is in increasing order.
- 13. Nearly, all metals combine with fluorine either in cold or on heating to form fluorides. Chlorine combines with a large number of metals but slowly. Bromine and iodine do not react with noble metals and even with less active metals. The reactivity of halogens towards metals decreases on moving down the group. The halides are predominantly ionic in nature. For a particular metal the ionic character decreases from F to I. With metals in higher oxidation states, the halides are covalent in nature.

Halogens also combine with a number of non-metals. The reactivity decreases from F to I.

- 14. Fluorine decomposes water very readily even in dark at low temperature, forming a mixture of O<sub>2</sub> and O<sub>3</sub>. Chlorine decomposes water in presence of sunlight while bromine decomposes water slowly in presence of sunlight. Iodine does not decompose water.
- 15. All the halogens react with hydrogen to form volatile covalent hydrides of the formula HX. The activity of halogens

toward hydrogen decreases from F to I. These hydrides are called hydracids or halogen acids.

- (a) The hydracids are formed by direct combination of halogens and hydrogen.
  - The aqueous solution of HF can be obtained by heating CaF<sub>2</sub> with conc. H<sub>2</sub>SO<sub>4</sub> in a lead retord. Hydrogen chloride can be prepared by NaCl with conc. H<sub>2</sub>SO<sub>4</sub>. However, HBr and HI cannot be prepared by heating bromides and iodides with conc. H<sub>2</sub>SO<sub>4</sub> because HBr and HI are strong reducing agents and oxidised by conc. H<sub>2</sub>SO<sub>4</sub> into Br<sub>2</sub> and I<sub>2</sub> respectively. HBr and HI are obtained by heating bromides and iodides with H<sub>3</sub>PO<sub>4</sub> or hydrolysis of corresponding phosphorus trihalides.
- (b) Except HF or H<sub>2</sub>F<sub>2</sub>, other halides are gases. They fume in air and have pungent odour. All are heavier than air. H<sub>2</sub>F<sub>2</sub> is a liquid due to association of molecules through hydrogen bonding. The boiling points vary as:

(c) The bond strength decreases from HF to HI. The decrease in stability is due to decrease in electronegativity. The dissociation energy of H—X bond decreases.

$$\frac{H - F}{136 \text{ kcal mol}^{-1}} > H - Cl > H - Br > H - I$$

- (d) The reducing nature increases from HF to HI. HF does not show reducing nature.
- (e) Dipole moment of these hydrides decreases from HF to HI.
- (f) Acidic nature of these hydrides is HI > HBr > HCl > HF.

  This is because of the fact that the strength of the conjugate base increases as:

$$I^- < Br^- < Cl^- < F^-$$

- (g) HCl, HBr and HI form one series of salts while hydrofluoric acid forms two series of salts MHF<sub>2</sub> and M<sub>2</sub>F<sub>2</sub> (M is monovalent).
- 16. Halogens and oxygen do not combine directly with each other. However, these compounds have been obtained indirectly. The known compounds are:

$$\begin{array}{cccc} OF_2 & Cl_2O & Br_2O & I_2O_5 \\ O_2F_2 & ClO_2 & BrO_2 & \\ & Cl_2O_6 & BrO_3 & \\ & Cl_2O_7 & \end{array}$$

The compounds of oxygen and fluorine are not called oxides but fluorides as fluorine is more electronegative than oxygen.

- (a) Oxides of Cl, Br and I are acidic and acidic character increases with increase of percentage of oxygen in them.
- (b) All the oxides of halogens are powerful oxidants, highly reactive and unstable towards heat. In general, higher oxides are relatively more stable than lower oxides for a particular halogen.
  - (c) Oxygen fluorides do not form oxyacids.
  - (d) In these oxides, bonds are mainly covalent due to small difference in the electronegativity of oxygen and halogens.

- (e) All the three monoxides, viz., OF<sub>2</sub>, Cl<sub>2</sub>O and Br<sub>2</sub>O have tetrahedral structure involving sp<sup>3</sup> hybridization of oxygen, bond angle increases with increase in size of the halogen atom.
- (f) Oxides of iodine I<sub>2</sub>O<sub>4</sub> and I<sub>4</sub>O<sub>9</sub> are not true oxides but iodates, IO(IO<sub>3</sub>) and I(IO<sub>3</sub>)<sub>3</sub> respectively.
- 17. Except fluorine, all other halogens form oxyacids of the type HXO, HXO<sub>2</sub>, HXO<sub>3</sub> and HXO<sub>4</sub>. Some of these acids are quite unstable.

- (a) All these acids are monobasic and the halogen atom is  $sp^3$  hybridized.
- (b) Acidic character increases with increase in oxidation number of the halogen.

(c) In any series, acidic character decreases as the electronegativity decreases.

$$HClO_4 > HBrO_4 > HIO_4$$

(d) Oxidising nature for the same halogen decreases.

(e) Stability for the same halogen increases.

$$HCIO' < HCIO_2 < HCIO_3 < HCIO_4$$

**18.** Fluorine reacts with cold dilute alkalies yielding OF<sub>2</sub> and with conc. alkalies evolve oxygen.

$$2F_2 + 2NaOH \longrightarrow 2NaF + OF_2 + H_2O$$
;  
 $Cold + dil$ .  
 $2F_2 + 4NaOH \longrightarrow 4NaF + O_2 + 2H_2O$   
 $Conc$ .

Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub> behave similarly towards alkalies. With dilute and cold alkalies form a mixture of halide and hypohalide while with hot and conc. alkalies form a mixture of halide and halate.

$$\begin{array}{c} {\rm 2NaOH} + X_2 \longrightarrow {\rm Na}X + {\rm Na}X{\rm O} + {\rm H_2O}; \\ {\rm Cold+dil.} & {\rm Hypohalite} \\ {\rm 6NaOH} + 3X_2 \longrightarrow {\rm 5Na}X + {\rm Na}X{\rm O_3} + {\rm 3H_2O} \\ {\rm Hot+conc.} & {\rm Halate} \end{array}$$

19. The halogens on account of difference in the electronegativities combine with each other to form compounds of the type  $AB_n$  where A is always bigger atom and B is smaller, atom and n may have values 1, 3, 5 and 7. These are covalent compounds and called interhalogen compounds.

AB type CIF, BrF, BrCl, ICl, IBr  

$$AB_3$$
 type CIF<sub>3</sub>, BrF<sub>3</sub>, ICl<sub>3</sub>  $\longrightarrow sp^3d$  hybridization of A.  
Two lone pairs  
 $AB_5$  type IF<sub>5</sub>, BrF<sub>5</sub>  $\longrightarrow sp^3d^2$  hybridization of A.  
One lone pair  
 $AB_7$  type IF<sub>7</sub>  $\longrightarrow sp^3d^3$  hybridization of A.

Interhalogen compounds are gases or liquids. These are volatile and fume in air. These compounds are more reactive

than halogens except fluorine because A—B bond is weaker than B—B bond. These are hydrolysed and act as oxidising agents.

20. Halide ions often react with molecules of halogens or interhalogens and form polyhalides.

$$I^- + I_2 \longrightarrow I_3^-$$

 $I_3^-$  (polyhalide) ion is stable in aqueous solution and in ionic crystals. More complex ions such as  $I_5^-$ ,  $I_7^-$  and  $I_9^-$  have been prepared. The  $Br_3^-$  and  $Cl_3^-$  ions are much less stable than  $I_3^-$ .

Many polyhalides are known in which two or three different halogens are present such as ICl<sub>2</sub>, ICl<sub>4</sub>, (IBrF) and (IBrCl).

21. Some of the monovalent ions made of electronegative atoms and possessing properties similar to halide ions are known which are called pseudohalide ions. The corresponding dimers having no charge of these pseudohalide ions are called pseudohalogens.

Pseudohalide ions
Cyanide ion (CN<sup>-</sup>)
Thiocyanate ion (SCN<sup>-</sup>)
Cyanate ion (OCN<sup>-</sup>)

Cyanate ion (OCN<sup>-</sup>)

Pseudohaliogens
(CN)<sub>2</sub> Cyanogen
(SCN)<sub>2</sub> Thiocyanogen
(OCN)<sub>2</sub> Oxycyanogen

- 22. The important minerals of fluorine are:
  - (i) Fluorspar (CaF<sub>2</sub>); (ii) Cryolite (Na<sub>3</sub>AlF<sub>6</sub>); (iii) Fluorapatite [CaF<sub>2</sub>·3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>]

In small amounts, it is present as fluorides in plant ashes, soil, sea water, bones and teeth of animals.

The isolation presented many difficulties. It was finally isolated by **Moissan** in 1886 by electrolysis of anhydrous hydrofluoric acid in potassium hydrogen fluoride (KHF<sub>2</sub>) using Pt–Ir vessel at –23°C. The electrodes used were also of Pt–Ir alloy.

In modern methods, fluorine is prepared by electrolysis of fused KHF<sub>2</sub>. The electrolytic cells are made of copper, nickel or monel metal. The anode is generally of graphite. The fluorine set free contains some carbon tetrafluoride. The methods used are: (i) Dennis and (ii) Whytlaw-Gray.

- 23. The fluorine compounds have wide applications:
  - (a) Freon, CF<sub>2</sub>Cl<sub>2</sub> (dichlorodifluoro methane) is used in refrigerators and cold storage plants.
  - (b) Teflon (C<sub>2</sub>F<sub>4</sub>)<sub>x</sub>, a new plastic, has a very high electrical resistance and is used as insulating material. It is not affected by acids, alkalies and strong oxidising agents.
  - (c)  $H_2F_2$  is used for etching of glass.
  - (d) SF<sub>6</sub> has insulating properties. It is used in X-ray and high voltage machines.
  - (e) NaF and Na<sub>3</sub>AlF<sub>6</sub> are used as insecticides.
  - (f) CuF<sub>2</sub> is used in ceramic industry.
  - (g) UF<sub>6</sub> is used for separation of U<sup>235</sup> isotope from natural uranium.
  - (h) Sodium fluoroacetate is used as a rat poison.
- 24. Chlorine was discovered by Scheele in 1774. The old name is oxymuriatic acid gas. Common salt (NaCl) is the most important chloride which occurs in sea water, lakes and in rocks. It is prepared (i) by oxidation of HCl with MnO<sub>2</sub>, PbO<sub>2</sub>,

Pb<sub>3</sub>O<sub>4</sub>, KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, O<sub>3</sub>, NaClO, etc. (ii) by heating dry platinum chloride (PtCl<sub>4</sub>) or gold chloride (AuCl<sub>3</sub>) in a hard glass tube. It gives pure chlorine.

The methods used for its manufacture are:

- (a) Weldon's process  $(MnO_2 + HCl)$  (b) Deacon's process-chlorine is obtained by air oxidation of HCl in presence of  $CuCl_2$  as a catalyst (c) Nitrosyl chloride process (d) By-product in the manufacture of caustic soda or sodium. Chlorine is stored and transported in liquid state.
- 25. Chlorine is a yellowish green gas with pungent suffocating and poisonous nature. It is fairly soluble in water. The aqueous solution is called chlorine water which gives crystals of chlorine hydrate (Cl<sub>2</sub>·8H<sub>2</sub>O) at 0°C. In presence of moisture, it acts as an oxidising and bleaching agent.
- 26. Chlorine is used in the manufacture of bleaching powder, chlorates, hypochlorites, HCl, chloroform, CCl<sub>4</sub>, phosgene (COCl<sub>2</sub>), tear gas (CCl<sub>3</sub>·NO<sub>2</sub>) and mustard gas (Cl—C<sub>2</sub>H<sub>4</sub>—S—C<sub>2</sub>H<sub>4</sub>—Cl). It is used in purification of drinking water and as a bleaching agent for cotton fabrics, paper and rayon.
- 27. Bromine was discovered by **Balard** in 1826. It is obtained either from the mother liquor obtained after crystallising KCl from carnallite or from sea water by passing Cl<sub>2</sub> gas. The vapours are absorbed in Na<sub>2</sub>CO<sub>3</sub> solution when a mixture of NaBr and NaBrO<sub>3</sub> is obtained which is distilled with H<sub>2</sub>SO<sub>4</sub> to recover bromine.
- **28.** Iodine was discovered by **Courtois** in 1812. Two main sources of iodine are:
  - (a) Deep sea-weeds' ashes known as kelp contains 0.5% iodine in the form of iodides.
  - (b) Caliche or crude chile saltpetre which contains 0.2% of NaIO<sub>3</sub>.
- **29.** I<sub>2</sub> is slightly soluble in water. The solubility can be increased by addition of KI.

$$KI + I_2 \longrightarrow KI_3$$
 (Soluble)

It is soluble in organic solvents such as chloroform, carbon tetrachloride, alcohol, ether, etc. It oxidises  $Na_2S_2O_3$  into sodium tetrathionate. This reaction is useful in iodometric titrations.

30. Tincture of iodine is a mixture of I<sub>2</sub> and KI dissolved in rectified alcohol. It is used as antiseptic. Iodex—a product containing iodine is used as antiseptic and analgesic. Although iodine does not displace chlorine or bromine from the solutions of their salts, yet it displaces them from their oxysalts.

$$2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2$$
  
 $2KBrO_3 + I_2 \longrightarrow 2KIO_3 + Br_2$ 

31. Bleaching powder (CaOCl<sub>2</sub>·H<sub>2</sub>O) is also called calcium chlorohypochlorite because it is a mixed salt of hydrochloric acid and hypochlorous acid. It is represented as:



It is obtained by the action of Cl2 on slaked lime.

Bleaching powder loses its chlorine content by the action of dilute acids or carbon dioxide. The amount of chlorine obtained from the sample of a bleaching powder by this way is termed **available chlorine**. A good sample of bleaching powder contains 35–38% of available chlorine.

On long standing bleaching powder undergoes autooxidation into calcium chlorate and calcium chloride.

$$6CaOCl_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2$$

The products do not have available chlorine. Thus, bleaching powder loses available chlorine with time.

- 32. When a chloride is heated with conc. H<sub>2</sub>SO<sub>4</sub> in presence of solid K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in a dry test tube, deep red vapours of chromyl chloride are evolved. When these vapours are passed through NaOH solution, the solution becomes yellow due to formation of sodium chromate. The solution is neutralised with acetic acid and on addition of lead acetate solution, a yellow precipitate of lead chromate is formed. This is a test of chloride ion and is known as chromyl chloride test.
- 33. Warming KClO<sub>3</sub> with conc. HCl gives a mixture of Cl<sub>2</sub> and ClO<sub>2</sub> known as euchlorine which is a bleaching agent.

- 34. Iodine shows electropositive nature as it has lowest ionisation potential among halogens. It has the tendency to lose electron or electrons to form I<sup>+</sup> and I<sup>3+</sup> cations. Compounds such as ICl, ICN, ICl<sub>3</sub>, IPO<sub>4</sub>, I(CH<sub>3</sub>COO)<sub>3</sub>, etc., are known.
- 35. Some of the products of halogens have been given special names.

$Mg(ClO_4)_2$		Anhydrone
KClO <sub>3</sub>		Berthelot's salt
KHF <sub>2</sub>	-	Ferming's salt
Aq. soln. of NaOCl		Javelle water
CaOCl <sub>2</sub> ·H <sub>2</sub> O	_	Bleaching powder
Cl <sub>2</sub> and ClO <sub>2</sub> mixture	-	Euchlorine
Soln. of HCl		Spirit of salt
CCl <sub>3</sub> ·NO <sub>2</sub>	_	Tear gas
$\mathbf{C}_{\mathbf{b}}$		Oxymuriatic acid gas

36. Cl<sub>2</sub> and F<sub>2</sub> do not react with starch solution. Br<sub>2</sub> gives yellow colour with starch solution and I<sub>2</sub> gives deep blue colour with starch solution.

# ••- PRACTICE PROBLEMS

## Subjective Type Questions

- 1. Name the element of group 17, which has the following properties:
  - (a) highest electron affinity
  - (b) strongest oxidising agent
  - (c) radioactive
  - (d) violet solid
  - (e) does not exhibit positive oxidation state
- 2. Among the hydrides of halogens predict the hydride having:
  - (a) highest boiling point
  - (b) strongest reducing agent
  - (c) most stable
  - (d) least acidic
  - (e) lowest boiling point
- 3. Complete and balance the following chemical reactions:
  - (i)  $I_2 + NaClO_3 \longrightarrow$
  - (ii)  $IO_3^- + I^- + H^+ \longrightarrow$
  - (iii)  $Br_2 + NaI \longrightarrow$
  - (iv)  $I_2 + S_2O_3^{2-} \longrightarrow$
  - (v)  $BrO_3^- + F_2 + OH^- \longrightarrow$
- 4. Answer the following:
  - (i) Write the general electronic configuration of halogens in the valence shell.
  - (ii) Name the halogens.
  - (iii) Name the radioactive (last) element of VIIA or 17th group.
  - (iv) Write the physical states of halogens under ordinary conditions.

- (v) Write the two important minerals of fluorine.
- (vi) Name four oxyacids of chlorine. Give their molecular formulae.
- (vii) Name the halogen which gives ozone with water.
- (viii) Name the oxide of chlorine which has odd number of electrons and paramagnetic in nature.
- (ix) Give one example each of the compound of chlorine in which it shows +1, -1, +3, +4, +5, +6 and +7 oxidation state.
- (x) Name the halogen which has highest bond energy amongst halogens.
- (xi) Name the compound which on electrolysis gives fluorine gas at anode.
- (xii) Name the fluoro carbon used in refrigerators.
- (xiii) Name two poisonous gases of chlorine used in the warfare.
- (xiv) What is the atomicity of halogens?
- (xv) What is the percentage of available chlorine in a good sample of bleaching powder?
- (xvi) Name two interhalogens of AB<sub>3</sub> type.
- (xvii) What are the constituents of tincture of iodine?
- (xviii) What is the colour of vapours obtained when an iodide is heated with conc. H<sub>2</sub>SO<sub>4</sub>?
- (xix) What is the shape of HClO<sub>4</sub>?
- (xx) What is the shape of ClF<sub>3</sub>?
- 5. Complete the following reactions and give balanced equations:
  - (i)  $Cl_2 + OH^- \longrightarrow \dots + ClO_3^- + \dots$
  - (ii)  $MnO_2 + HCl \longrightarrow MnCl_2 + \dots + \dots$

- - (xi)  $H_2SO_4 + HI \longrightarrow \dots + \dots + \dots$ [Roorkee 1998]

(xii)  $CaOCl_2+NaI+HCl \longrightarrow .....+CaCl_2+H_2O+NaCl$ [Roorkee 1998]

- 6. What happens when? (Give balanced equations)
  - (i) Sodium iodate is treated with sodium bisulphite solution.
  - (ii) Chlorine is passed through hot NaOH solution.
    [M.L.N.R. 1990]
  - (iii) Chlorine is passed into aqueous potassium hydroxide.
  - (iv) Chlorine gas is bubbled through a solution of ferrous bromide.
  - (v) Iodine reacts with conc. HNO<sub>3</sub>. [M.L.N.R 1992]
  - (vi) Chlorine is passed over slaked lime.
  - (vii) Sodium chloride is heated with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and conc. H<sub>2</sub>SO<sub>4</sub>. [I.I.T. 1990]
  - (viii) Potassium iodide is heated with MnO<sub>2</sub> and conc. H<sub>2</sub>SO<sub>4</sub>.
  - (ix) Chlorine reacts with Na<sub>2</sub>SO<sub>3</sub> solution.
  - (x) Iodine is added to stannous chloride solution.
  - (xi) Chlorine is passed through a suspension of iodine.
  - (xii) Cl<sub>2</sub> is passed through a suspension of CaCO<sub>3</sub>.
  - (xiii) Chlorine gas is passed through dry and aqueous sulphur dioxide.
  - (xiv) Bromine reacts with Na<sub>2</sub>CO<sub>3</sub> solution.
  - (xv) Potassium iodide is added to bleaching powder containing dilute acetic acid.

#### 7. Arrange the following:

- (a) HClO<sub>2</sub>, HClO<sub>3</sub>, HClO<sub>4</sub> in increasing order of thermal stability.
- (b) HClO<sub>2</sub>, HClO<sub>3</sub>, HClO<sub>4</sub> in order of increasing acid strength.
- (c) HClO<sub>2</sub>, HClO<sub>3</sub>, HClO<sub>4</sub> in order of increasing oxidising power.
- (d) F, Cl, Br, I in order of increasing reducing nature.
- (e) I<sub>2</sub>, HI, HIO<sub>4</sub>, ICl in order of increasing oxidation number of iodine.
- (f) HOF, HOCl, HOBr, HOI in order of increasing acid strength.
- (g) F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> in order of increasing oxidising power.
- (h) HF, HCl, HBr, HI in order of increasing acid strength.

- (i) F, Cl, Br, I in order of increasing electronegativity or reactivity.
- (j) F, Cl, Br, I in order of increasing electron affinity.
- **8.** Write chemical formula and uses of the following:
  - (i) Muriatic acid (ii) Freon (iii) Hypo solution
  - (iv) Caliche (v) Kelp (vi) Bleaching powder.
- 9. Give equations only:
  - (i) How chlorine is obtained from the following substances?
     (a) HCl
     (b) NaCl
     (c) KClO<sub>3</sub>
     (d) Bleaching powder
  - (ii) How bromine is obtained from the following substances? (a) NaBrO<sub>3</sub> (b) HBr (c) KBr
  - (iii) How iodine is obtained from the following substances?
    (a) KI (b) NaIO<sub>3</sub> (c) HI
- 10. What is the oxidation number of the various halogen atoms present in the following?
  - (i) CIF (ii) ICl (iii) PCl<sub>5</sub> (iv) Cl<sub>2</sub> (v) KClO<sub>3</sub> (vi) KClO<sub>4</sub> (vii) HClO<sub>2</sub> (viii) Cl<sub>2</sub>O (ix) F<sub>2</sub>O (x) Cl<sub>2</sub>O<sub>7</sub>.
- 11. What is the geometry and hybridization of the central atom of the following molecules or ions?
  - (i)  $ClO_2^-$  (ii)  $ClO_3^-$  (iii)  $IF_7$  (iv)  $ICl_2^-$  (v)  $ICl_4^-$  (vi)  $Cl_2O$  (vii)  $IF_3$  (viii)  $ClO_2$ .
- 12. Write short notes on:
  - (i) Available chlorine.
  - (ii) Interhalogen compounds.
  - (iii) Pseudohalogens.
  - (iv) Basic properties of iodine.
  - (v) Use of bleaching powder in textile industry.
  - (vi) Relative acid strength of the hydracids of halogens.
  - (vii) Relative oxidising nature of halogens.
  - (viii) Relative acid strength of the oxyacids of chlorine.
- 13. (i) Describe the iodometric method for estimating available chlorine in the given sample of bleaching powder.
  - (ii) Give the chemistry of the test of fluoride.
  - (iii) Give the chemistry of chromyl chloride test.
  - (iv) Give the chemistry of chloroform test for the detection of bromide and iodide ions.
- 14. Explain the following with proper reason:
  - (i) Fluorine cannot be prepared from fluorides by chemi cal oxidation.

[Hint: The standard reduction potential of fluorine is maximum.

$$: F \cdot + e^{-} \longrightarrow : F : -$$

Thus, it cannot be oxidised by any other reagent. F<sup>-</sup> ion is very stable due to small size and high electronegativity of fluorine atom.]

(ii) Anhydrous HCl is a bad conductor of electricity while aqueous HCl is a good conductor. [I.I.T. 1995]
 [Hint: In anhydrous state, HCl is a covalent molecule. In aqueous solution, HCl combines with water molecule to form H<sub>3</sub>O<sup>+</sup> and Cl<sup>-</sup> ions.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

(iii) Halogens are coloured.

[Hint: Halogens absorb part of the light in the visible region which cause excitation of outer electrons to higher energy levels. The excitation energy depends on the size of the halogen atom, the smaller the atom, the greater is the excitation energy. Thus, fluorine absorbs violet light and thus appears yellow (complementary colour). As different colours are absorbed by halogens, they display different complementary colours also.]

(iv) Halogens are strong oxidising agents.

[Hint: Halogens act as strong oxidising agents because they have high tendency to accept electron, *i.e.*, they have high electron affinity values. Their reduction potentials are high (positive) and decrease from F to I. Thus, oxidising nature decreases from F to I.]

(v) When a blue litmus is dipped into a solution of hypochlorous acid, it first turns red and then later gets decolourised.

[Hint: HClO is an acid, thus turns blue litmus into red. HClO is also an oxidising agent. The nascent oxygen given by HClO bleaches the red litmus.

Red litmus + 
$$O \longrightarrow Colourless$$
]

(vi) The bleaching action of chlorine is permanent while that of sulphur dioxide is temporary.

[Hint: Chlorine bleaching action is due to oxidation while that of sulphur dioxide is due to reduction. Hence, the substance bleached by SO<sub>2</sub> is reoxidised by the oxygen of the air to its original state.]

(vii) The brown colour of an acidified dilute solution of iodine in aqueous potassium iodide is intensified by addition of a nitrite but is discharged by the addition of sulphite.

[Hint: Nitrite ions oxidise iodide ions to iodine and thus brown colour is intensified.

$$4H^+ + 2NO_2^- + 2I^- \longrightarrow 2NO + I_2 + 2H_2O$$
  
Iodine acts as an oxidising agent with sulphite and converted into  $I^-$ , *i.e.*, the solution becomes colourless.

$$I_2 + SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2\Gamma$$

(viii) Fluorine is a non-metal whereas iodine shows some metallic properties as well.

[Hint: Ionisation potential decreases on moving down from F to I. The iodine can lose electron/electrons and form positive ions and hence shows metallic character.]

(ix) Colour of potassium iodide solution containing starch turns blue when chlorine water is added.

[Hint: Chlorine being more reactive displaces iodine from KI. Iodine is absorbed by starch and thus blue colour is developed.

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$
  
 $I_2 + Starch \longrightarrow Blue colour$ 

(x) Pure HI kept in a bottle acquires a brown colour after sometime. [Hint: HI is a strong reducing agent. It is even oxidised by oxygen of the air. The iodine is liberated which is dissolved imparting a brown colour to solution.]

(xi) Iodine dissolves more in KI solution than in water.

#### [Dhanbad 1992]

[Hint: I<sub>2</sub> is a covalent molecule. Thus, its solubility is less in polar solvent, *i.e.*, water. Potassium iodide combines with iodine and forms a polyhalide which is an ionic compound. Being ionic, KI<sub>3</sub> is more soluble.

$$KI + I_2 \longrightarrow KI_3(K^+I_3)$$

(xii) Iodine is liberated in the reaction between KI and Cu<sup>2+</sup> but chlorine is not liberated when KCl is added to Cu<sup>2+</sup> ion.

[Hint: I ion is a strong reducing agent. It reduces Cu<sup>2+</sup> ion to Cu<sup>+</sup> ion. The Cl ion is a weak reducing agent. Thus, it does not reduce Cu<sup>2+</sup> ion.

$$2Cu^{2+} + 4KI \longrightarrow Cu_2I_2 + I_2 + 4K^+$$

(xiii) KHF<sub>2</sub> is well known whereas KHCl<sub>2</sub> or KHBr<sub>2</sub> does not exist.

[Hint: Hydrofluoric acid exists as dimeric molecule (H<sub>2</sub>F<sub>2</sub>) due to hydrogen bonding. It, thus, exhibits dibasic nature and forms two series of salts, KHF<sub>2</sub> as [K<sup>+</sup> and F<sup>-</sup> - - - H—F] and KF[K<sup>+</sup> and F<sup>-</sup>]. HCl and HBr exist as monomeric molecules as hydrogen bonding is not present.]

(xiv) A fresh iodine stain can be removed by washing with hypo solution.

[Hint: Hypo reacts with iodine to form water soluble colourless sodium tetrathionate and sodium iodide.

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

(xv) Dry chlorine does not bleach clothes.

[Hint: The bleaching action of chlorine is due to the liberation of nascent oxygen from water (moisture).

$$H_2O + Cl_2 \longrightarrow 2HCl + (O)$$

(xvi) Ferric iodide is very unstable but ferric chloride is stable.

[Him: I<sup>-</sup> ion is a strong reducing agent. Iodide thus reduces ferric into ferrous. Cl<sup>-</sup> ion is a weak reducing agent and does not reduce Fe<sup>3+</sup> to Fe<sup>2+</sup>.]

(xvii) HF is least volatile and HCl is most volatile amongst hydrogen halides.

[Hint: In covalent compounds, the boiling point increases with increase of molecular mass as van der Waals' forces increase. The volatility thus, decreases in covalent compounds with increase in molecular mass. However, hydrogen bonding is present in HF. Due to which, the boiling point of HF is higher and the volatility is less. Thus, the volatility of hydrogen halides can be represented as:

(xviii) Fluorine does not form  $F_3^-$  (polyhalide) ion.

[Hint: No d-orbitals are present in fluorine while d-orbitals are present in other halogens. The formation of  $X_3^-$  ion involves  $sp^3d$  hybridization.]

(xix) Fluorine gives fumes with moist air.

[Hint: Fluorine reacts with water to form HF.

$$2H_2O + 2F_2 \longrightarrow 4HF + O_2$$

HF, being liquid, absorbs liquid droplets to form

(xx) Interhalogens are more reactive than halogens.

[Hint: The bond in the interhalogen A - X is weaker than X—X bond in the halogens. This is on account of less effective overlapping between orbitals of dissimilar atoms than those of similar atoms.]

(xxi) HF is not stored in glass bottles but kept in wax

[Hint: HF attacks glass bottles. The sodium and pota--ssium-silicates-are-converted-into-fluorosilicates.

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$$

(xxii) HF has a greater electronegativity difference and more ionic character than HCl, HBr and HI but it is the weakest acid.

Hint: The weakest acidic nature of HF is due to following three factors:

- (i) Strong H-F bond as the dissociation energy
- (ii) Large heat of dehydration due to hydrogen bonding.
- (iii) Low value of electron affinity.]
- 15. The following statements are correct under certain conditions. Mention the conditions.
  - (i) Chlorine is a good bleaching agent.
  - (ii) A mixture of H<sub>2</sub> and Cl<sub>2</sub> explodes.
  - (iii) Cl2 reacts with NaOH solution to produce sodium chloride and sodium hypochlorite (along with water).
  - (iv) Cl2 reacts with NaOH solution to produce sodium chloride and sodium chlorate (along with water).
  - (v) Cl<sub>2</sub> substitutes hydrogen atoms of a molecule of methane.
  - (vi) Cl<sub>2</sub> reacts with ammonia to form nitrogen and ammonium chloride.
  - (vii) Cl<sub>2</sub> reacts with lime to form bleaching powder.
  - (viii) Iodine dissolves freely in water.
  - (ix) Chlorine forms an addition product with SO<sub>2</sub>.
- 16. A black powder when heated with NaCl and conc. H<sub>2</sub>SO<sub>4</sub> gives off a greenish yellow gas. The gas on passing through liquor ammonia liberates N2 and on passing through boiling KOH yields compounds one of which when heated with the black powder evolves oxygen. Name the gas and the black

- powder. Explain the chemical reactions involved with
- 17. A sodium salt is heated with concentrated sulphuric acid. The evolved gas is found to turn moist litmus paper red and produce white fumes in contact with a glass rod moistened with ammonia solution. It also gives white precipitate when passed through AgNO3 solution. When the salt is heated with MnO<sub>2</sub> and conc. H<sub>2</sub>SO<sub>4</sub>, a gas with an irritating smell is evolved which turns starch-iodide paper blue. Identify the salt and the gaseous product evolved from it. Explain your answer with relevant chemical equations.
- 18. A certain compound (X) shows the following reactions.
  - (i) When KI is added to an aqueous suspension of (X)containing acetic acid, iodine is liberated.
  - (ii) When CO<sub>2</sub> is passed through an aqueous suspension of (X), the turbidity transforms to a precipitate.
  - (iii) When the paste of (X) in water is heated with ethyl alcohol, a product of anaesthetic use is obtained. Identify (X) and write down chemical equations for reactions at step (i), (ii) and (iii). [Roorkee 1992]
- 19. A colourless inorganic compound imparts a green colour to flame. It's solution does not give any precipitate with H2S. It's solution gives white precipitate with H<sub>2</sub>SO<sub>4</sub>. When it is heated with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and conc. H<sub>2</sub>SO<sub>4</sub>, a red gas is evolved. The gas when passed through aqueous NaOH solution turns it yellow. Identify the compound and give chemical reactions.

## Matching Type Questions

#### Match the following:

[A]

(i) Fluorine

(a) Carnallite

(ii) Chlorine

(b) Hydrogen bonding

(iii) Bromine

(c) Beckmann's process

(iv) Iodine

(d) Reducing agent

(v) Bleaching powder

(e) Pseudohalogen

(vi) HF

(f) Dennis process

(vii) HI

(g) Sea-weeds

(viii) (CN)2

(h) Deacon's process

B

(i) Moissan

(a) Chlorine

(ii) Scheele

(b) Bleaching powder

(iii) Balard

(c) Iodine

(iv) Courtois

(d) Fluorine

(v) Odling

(e) Bromine

## tuswers

**Answers:** Subjective Type Questions

- 1. (a) Cl (b) F (c) At (d) I (e) F
- (a) HF (b) HI (c) HF (d) HF (e) HCl
- 3. (i)  $I_2 + 2NaClO_3 \longrightarrow 2NaIO_3 + Cl_2$ 
  - (ii)  $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$
  - (iii)  $Br_2 + 2NaI \longrightarrow 2NaBr + I_2$
  - (iv)  $I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^{-}$
  - (v)  $BrO_3^- + F_2 + 2OH^- \longrightarrow BrO_4^- + 2F^- + H_2O$
- **4.** (i)  $ns^2np^5$  (ii) Fluorine, chlorine, bromine, iodine (iii) Astatine (iv) Fluorine and chlorine are gases, bromine is liquid and iodine is solid. (v) Fluorspar (CaF2); cryolite (Na3AlF6) (vi) Hypochlorous acid (HClO), Chlorous acid (HClO2); Chloric acid (HClO3); Perchloric acid (HClO<sub>4</sub>) (vii) Fluorine (viii) Chlorine dioxide, ClO<sub>2</sub> (ix) Cl<sub>2</sub>O (+1), HCl (-1), ClF<sub>3</sub> (+3), ClO<sub>2</sub> (+4), HClO<sub>3</sub> (+5), Cl<sub>2</sub>O<sub>6</sub> (+6), HClO<sub>4</sub> (+7) (x) chlorine (xi) Fused anhydrous potassium hydrogen fluoride (KHF2) (xii) Freon (CF2Cl2)

(iv)

Caliche

NaIO<sub>3</sub>

(main constituent) iodine

For the manufacture of

In small amount for the

NaI

(v)

Kelp

```
(xiii) Phosgene (COCl<sub>2</sub>), Tear gas (CCl<sub>3</sub>NO<sub>2</sub>) (xiv) two
    (xv) 35–38% (xvi) Chlorine trifluoride (ClF<sub>3</sub>); iodine trichloride (ICl<sub>3</sub>)
     or I<sub>2</sub>Cl<sub>6</sub>) (xvii) Iodine, potassium iodide and ethyl alcohol
     (xviii) Violet (xix) Tetrahedral (xx) T-shaped.
                3Cl_2 + 6OH \longrightarrow 5CI + ClO_3 + 3H_2O
5.
               MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O
    (iii) NH_3 + 3Cl_2(Excess) \longrightarrow NCl_3 + 3HCl
    (iv) 2KMnO_4 + 10KCl + 8H_2SO_4 \longrightarrow
                                      6K_2SO_4 + 2MnSO_4 + 5Cl_2 + 8H_2O
           K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2
     (v)
    (vi)
               2CuSO_4 + 4KI \longrightarrow 2K_2SO_4 + Cu_2I_2 + I_2
            2NH_3 + 3NaOCl \longrightarrow 3NaCl + N_2 + 3H_2O
   (vii)
   (viii) 2Cl_2 + H_2O + 2HgO \longrightarrow 2HClO + HgO \cdot HgCl_2
    (ix) P_4 + 6I_2 + 12H_2O \longrightarrow 4H_3PO_3 + 12HI
     (x) 2NaBr + MnO_2 + 3H_2SO_4 -
                                         2NaHSO_4 + MnSO_4 + 2H_2O + Br_2
                H_2SO_4 + 2HI \longrightarrow I_2 + SO_2 + 2H_2O
     (xi)
    (xii) CaOCl_2 + 2NaI + 2HCl \longrightarrow I_2 + CaCl_2 + H_2O + 2NaCl
6. (i)2NaIO<sub>3</sub> + 5NaHSO<sub>3</sub> \longrightarrow 3NaHSO<sub>4</sub> + 2Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O + I<sub>2</sub>
     (ii)3Cl_2 + 6NaOH(conc.) \xrightarrow{Hot} 5NaCl + NaClO_3 + 3H_2O
           Cl_2 + 2KOH(aq.) \longrightarrow KCl + KClO + H_2O
               2FeBr_2 + 3Cl_2 \longrightarrow 2FeCl_3 + 2Br_2
     (iv)
                I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O
     (v)
               Ca(OH)_2 + Cl_2 \longrightarrow Ca(OCl)Cl + H_2O
     (vi)
    (vii)4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow
                                 2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O
   (viii) 2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2
     (ix) Cl_2 + Na_2SO_3 + H_2O \longrightarrow 2HCl + Na_2SO_4
      (x) SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI
     (xi) I_2 + 5CI_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCI
              2CaCO_3 + 2Cl_2 \longrightarrow CaCl_2 + Ca(ClO)_2 + 2CO_2
    (xii)
                     SO_2 + Cl_2 \longrightarrow SO_2Cl_2
    (xiii)
           SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl
           3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2
    (xiv)
                     (Conc. and hot)
    (xv) CaOCl_2 + 2CH_3COOH + 2KI \longrightarrow
                                         (CH_3COO)_2Ca + 2KCl + I_2 + H_2O
7. (a) HCIO < HCIO_2 < HCIO_3 < HCIO_4
      (b) HCIO < HCIO_2 < HCIO_3 < HCIO_4
      (c) HClO_4 < HClO_3 < HClO_2 < HClO
      (d) F^- < Cl^- < Br^- < l^-
      (e) HI < I_2 < ICI < HIO_4
      (f) HOI < HOBr < HOCl < HOF
      (g) I_2 < Br_2 < Cl_2 < F_2
      (h) HF < HCl < HBr < HI
      (i) I < Br < Cl < F
      (i) I < Br < F < Cl
                                                  Laboratory agent
     (i)
             Muriatic acid
                                    HCl
                                                  As an acid
      (ii)
                                                  As a refrigerant
                 Freon
                                  CF<sub>2</sub>Cl<sub>2</sub>
      (iii)
              Hypo soln.
                                                  (i) Used in photography
                                 Na_2S_2O_3
                                                  (ii) As a volumetric reagent
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manufacture of iodine
     (vi) Bleaching powder CaOCl2
                                              As a bleaching agent and
9. (i) (a) By heating conc. HCl with manganese dioxide.
               MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2
     (b) By doing electrolysis of NaCl solution.
     (c) By treating KClO3 with iodine.
                 2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2
     (d) Bleaching powder is treated either with mineral acids or CO<sub>2</sub>.
            CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2
              CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2
      (ii) (a) By heating mixture containing NaBr and NaBrO3 with
              hydrochloric acid.
               5\text{NaBr} + \text{NaBrO}_3 + 6\text{HCl} \longrightarrow 6\text{NaCl} + 3\text{Br}_2 + 3\text{H}_2\text{O}
      (b) By heating HBr with MnO<sub>2</sub>
               MnO_2 + 4HBr \longrightarrow MnBr_2 + Br_2 + 2H_2O
          or by passing Cl2 through HBr.
                  Cl_2 + 2HBr \longrightarrow 2HCl + Br_2
      (c) By heating KBr with MnO2 and conc. H2SO4 or by passing
          Cl2 through KBr solution.
      (iii) (a) By heating mixture of KI and MnO<sub>2</sub> with conc. H<sub>2</sub>SO<sub>4</sub> or
              by treating KI with H2O2.
                         2KI + H_2O_2 \longrightarrow 2KOH + I_2
          (b) Sodium iodate is treated with calculated quantity of sodium
              bisulphite.
        2NaIO_3 + 5NaHSO_3 \longrightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2
          (c) By passing Cl2 through HI.
                    2HI + Cl_2 \longrightarrow 2HCl + I_2
10. (i) Cl = +1, F = -1 (ii) I = +1, Cl = -1 (iii) Cl = -1 (iv) Cl = 0
      (v) +5 (vi) Cl = +7 (vii) Cl = +3 (viii) Cl = +1 (ix) F = -1
11. (i) Angular, sp^3 hybridization of Cl-atom
     (ii) Pyramidal, sp<sup>3</sup> hybridization of Cl-atom
    (iii) Pentagonal bipyramidal, sp^3d^3 hybridization of I-atom
    (iv) Linear, sp^3d hybridization of I-atom
     (v) Square planar, sp^3d^2 hybridization of I-atom
    (vi) V-shaped, sp<sup>3</sup> hybridization of O-atom
    (vii) T-shaped, sp^3d hybridization of I-atom
   (viii) Angular, sp^3d hybridization of Cl-atom.
12. See text
13. See text
15. (i) In presence of moisture (ii) On exposure to direct sunlight
      (iii) When NaOH solution is cold and dilute (iv) When NaOH
      solution is concentrated and hot (v) In diffused sunlight (vi) When
      NH3 is in excess (vii) When Cl2 is passed over dry slaked lime
      (viii) When KI is present (ix) When both are dry.
16. The black powder is MnO<sub>2</sub> and greenish-yellow gas is chlorine.
   MnO_2 + 2NaCl + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + Cl_2 + 2H_2O
                 3Cl_2 + 8NH_3 \longrightarrow N_2 + 6NH_4Cl
                3Cl_2 + 6KOH \longrightarrow KClO_3 + 5KCl + 3H_2O
           2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2 + [MnO_2]
```

17. The salt is NaCl and the evolved gas is HCl.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$HCl + Blue litmus \longrightarrow Red litmus$$

$$HCl + NH_3 \longrightarrow NH_4Cl$$

$$White fumes$$

$$HCl + AgNO_3 \longrightarrow AgCl + HNO_3$$

$$White ppt.$$

$$2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

$$Turns starch iodide paper blue.$$

$$18. The compound (X) is bleaching powder, CaOCl_2.$$

$$(i) CaOCl_2 + 2CH_3COOH + 2KI \longrightarrow Ca(CH_3COO)_2 + 2KCl + H_2O + I_2$$

$$(ii) CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

$$(iii) Ca(OCl)Cl + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

```
C_2H_5OH + Cl_2 \longrightarrow CH_3CHO + HCl
               CH<sub>3</sub>CHO + 3Cl<sub>2</sub> → CCl<sub>3</sub>CHO + 3HCl
           2CCl<sub>3</sub>CHO + Ca(OH)<sub>2</sub> ---- 2CHCl<sub>3</sub> + (HCOO)<sub>2</sub>Ca
19. The compound is BaCl<sub>2</sub>.
                BaCl<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub> -
                                           \rightarrow BaSO<sub>4</sub> + 2HCl
                                              White ppt.
           2BaCl_2+ K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow
                                          K_2SO_4 + 2CrO_2Cl_2 + 2BaSO_4 + 3H_2O
             CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O
Answers: Matching Type Questions
       [A] (i-f); (ii-h); (iii-a); (iv-g); (v-c); (vi-b); (vii-d); (viii-e).
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[B] (i-d); (ii-a); (iii-e); (iv-c); (v-b).

## ILLUSTRATIONS OF OBJECTIVE QUESTIONS

- 1. The property of halogen acids, that indicated incorrect is: (a) HF > HCl > HBr > HI . . . . acidic strength (b) HI > HBr > HCl > HF . . . . reducing strength (c) HI > HBr > HCl > HF . . . . bond length (d) HF > HCl > HBr > HI . . . . thermal stability [Hint: HI is the strongest acid while HF is the weakest acid. The order of acidic strength is: HI > HBr > HCl > HF ] 2. The property of halogens, that indicated incorrect is:
- - (a)  $F > Cl > Br > I \dots$  ionisation energy
  - (b)  $F > Cl > Br > I \dots$  electron affinity
  - (c)  $F > Cl > Br > I \dots$  electronegativity
  - (d)  $I > Br > Cl > F \dots$  density in liquid state

[Hint: The electron affinity of Cl is maximum. The trend is: Cl > F > Br > I

- 3.  $I_4O_9$  is a/an:
  - (a) covalent compound
- (b) coordinate compound
- (c) ionic compound
- (d) double salt

Ans. (c)

[Hint: I4O9 is actually I(IO3)3 which gets ionised.

$$I(IO_3)_3 \rightleftharpoons I^{3+} + 3(IO_3)^- ]$$
Cold and dilute NaOH  $\rightarrow$  (A) + NaCl + H<sub>2</sub>O

Hot and conc. NaOH  $\rightarrow$  (B) + NaCl + H<sub>2</sub>O

Compounds (A) and (B) are:

- (a) NaClO<sub>3</sub>, NaClO
- (b) NaOCl<sub>2</sub>, NaOCl
- (c) NaClO<sub>4</sub>, NaClO<sub>3</sub>
- (d) NaOCl, NaClO<sub>3</sub>

Ans. (d)

[Hint: 
$$Cl_2 + 2NaOH \longrightarrow NaCl + NaOCl + H_2O$$
  
Cold and dil. (A)

$$3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$
 ]

- 5. When chlorine water is added to an aqueous solution of sodium halide in the presence of chloroform, a violet colouration is obtained. When more of chlorine water is added, the violet colour disappears and solution becomes colourless. This confirms that sodium halide is :
  - (a) chloride
- (b) fluoride
- (c) bromide
- (d) iodide

Ans: (d)

 $\begin{array}{c} 2NaI + Cl_2 \longrightarrow 2NaCl + I_2 \text{ (violet colouration);} \\ I_2 + 5Cl_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl] \end{array}$ Hint:

- 6. As the atomic number of the halogens increases, the
  - (a) lose the outermost electrons less readily
  - (b) become less dense
  - (c) become lighter in colour
  - (d) gain electrons less readily

[Hint: The electron affinity decreases down the group as atomic size increases.]

- 7. The halogen that is most readily reduced is:
  - (a) fluorine
- (b) chlorine
- (c) bromine
- (d) iodine

Ans. (a)

[Hint: The reduction potential of fluorine is maximum and thus, it is easily reduced, i.e., it acts as strongest oxidising agent.]

- 8. Which has maximum pH in aqueous solution?
  - (a) NaClO
- (b) NaClO<sub>2</sub>
- (c) NaClO<sub>3</sub>
- (d) NaClO<sub>4</sub>

Ans. (a)

[Hint: NaClO+H2O \rightarrow NaOH + HClO; HClO is the weakest acid among the oxyacids of chlorine and thus, the solution of NaClO has maximum pH.1

				, ,	
9.	In the known interhalogen compounds, the maximum number of halogen atoms are:  (a) 4 (b) 8  (c) 5 (d) 7  Ans. (b)	15.	What products are experienced reaction of hypochlorous action (a) HClO <sub>3</sub> and Cl <sub>2</sub> O (c) HCl and Cl <sub>2</sub> O Ans. (d)	cid? [A.I.E.E. 20 (b) HClO <sub>2</sub> and HClO <sub>4</sub> (d) HCl and HClO <sub>3</sub>	
10.	shaking chlorine water with freshly precipitated yellow oxide of mercury?  (a) HClO <sub>3</sub> (b) HClO <sub>2</sub> (c) HClO (d) HClO <sub>4</sub> Ans. (c)  [Hint: HgO + 2Cl <sub>2</sub> + H <sub>2</sub> O	16.	[Hint: 3HClO \to HClO_3 + The number of lone pairs of e of ClF_3 is:  (a) 0 (b) 1  Ans. (c)  [Hint: Cl in first excited state	electrons present in central at [J.E.E. (Orissa) 20 (c) 2 (d) 3 $3d$	
11.	The substance, which is solid at room temperature, forms ionic compounds and reacts with hydrogen forming a hydride, the aqueous solution of which is acidic, may be:  (a) Al  (b) Na  (c) I <sub>2</sub> (d) Br <sub>2</sub>	17.		g agent because it has: [M.P.(P.M.T.) 20	/
12.	[Hint: Iodine is a solid at room temperature, can form ionic compounds. It forms HI with hydrogen which is an acid in aqueous solution.]  Interhalogen compounds are more reactive than the individual halogen because:  (a) two halogens are present in place of one (b) their bond energy is less than the bond energy of the		When $F_2$ reacts with hot and be obtained: (i) $OF_2$ (ii) $O_2$ (iii) $H_2O$ (a) (i), (iii) and (iv) (c) (ii), (iii) and (iv) Ans. (c) [Hint: $4NaOH + 2F_2 \longrightarrow 4$	conc. alkali, then following v [M.H.(C.E.T.) 20 (iv) NaF (b) (ii) and (iii) only (d) all of these	will
13.		19.	The hybridization present in (a) $sp^3d$ (c) $sp^3d^2$ Ans. (a)	in IF <sub>3</sub> is: [P.M.T. (Raj.) 20 (b) $sp^3$ (d) $sp^3d^3$	<del>105</del> ]
14.	<ul> <li>(a) aqueous solution of I<sub>2</sub></li> <li>(b) solution of iodine in aqueous KI</li> <li>(c) alcoholic solution of I<sub>2</sub></li> <li>(d) aqueous solution of KI</li> <li>Ans. (b)</li> <li>Which two of the following substances are used for</li> </ul>	20.	Shape of ClF <sub>3</sub> is:  (a) equilateral triangle  (c) V-shaped  Ans. (d)	(b) pyramidal (d) T-shaped	107]
	preparing iodized salt?  (i) KIO <sub>3</sub> (ii) KI (iii) I <sub>2</sub> (iv) HI  (a) (i) and (ii) (b) (i) and (iii)  (c) (ii) and (iv) (d) (iii) and (iv)  Ans. (a)	21.	Predict the product of the form $Cl_2 + HgO \longrightarrow$ (a) $HgCl_2 + O_2$ (c) $HgCl_2 + Cl_2O$ Ans. (c)	. =	107]

# JECTIVE QUESTIONS



set.	1: This set contains qu	iestions with only one corr	ect an	iswer	•		
1.	Halogens are:			14.	The solubility of iodine	in H <sub>2</sub> O may be increased by	the
	(a) gases under ordinary	conditions			addition of:		
	(b) electronegative in nat	ure			(a) $Na_2S_2O_3$	☐ (b) CHCl <sub>3</sub>	
	(c) fuming liquids				(c) KI	$\Box$ (d) $CS_2$	
	(d) the gases found in at	mosphere		15.	The colour of iodine solu	tion is discharged by shaking	with:
2.	Halogens show usually:	_			(a) aqueous sulphur diox		
	(a) electro-valency				(b) sodium sulphide		
	(b) covalency				(c) sodium sulphate	☐ (d) sodium chloride	
	- · · ·	and_covalency		16.	• •	through concentrated hot sol	ution
	(d) coordinate valency	-			of KOH, the compound f		
3.	The most powerful oxidisi	ng agent is: [C.B.S.E. (P.M.T.) 20	109]		(a) KClO	□ (b) KClO <sub>2</sub>	
		☐ (b) chlorine			(c) KClO <sub>3</sub>	☐ (d) KClO <sub>4</sub>	
	(c) bromine	☐ (d) iodine		17.	• •	he laboratory by the action of	:
4.	How many electrons are	present in the outermost orbi	t of		(a) Zn and HCl	☐ (b) CaCO <sub>3</sub> and HCl	
	halogens?				(c) Pb(NO <sub>3</sub> ) <sub>2</sub> and HCl	☐ (d) MnO <sub>2</sub> and HCl	
	(a) 1	□ (b) 3		18.	Which among the follow		
	(c) 5	□ (d) 7		10.	(a) Cl <sub>2</sub> O <sub>7</sub>	(b) Cl <sub>2</sub> O <sub>6</sub>	
5.	Which one of the hydrac	ids does not form any precipi	tate		(a) Cl <sub>2</sub> O <sub>7</sub> (c) ClO <sub>2</sub>	☐ (d) Cl <sub>2</sub> O <sub>6</sub>	
	with AgNO <sub>3</sub> ?			10	Pure chlorine is obtained		
	(a) HF	☐ (b) HCl		17.		1.	
	(c) HBr	□ (d) HI			(a) by heating PtCl <sub>4</sub>	th HCl	
6.	The strongest reducing a	gent is:			(b) by heating MnO <sub>2</sub> wit		
	(a) F <sup>-</sup>	□ (b) Cl <sup>−</sup>			(c) by treating bleaching	<del>-</del>	
	(c) Br	□ (d) I <sup>-</sup>		20		NaCl and MnO <sub>2</sub> with conc.H <sub>2</sub> S	$O_4$ $\square$
7.	Which one of the follow	ing is the strongest acid?		20.	Chlorine gas is dried over		J===-4
	(a) HF	□ (b) HI			(a) CaO	□ (b) NaOH	
	(c) HBr	☐ (d) HCl		•	(c) H <sub>2</sub> SO <sub>4</sub>	☐ (d) HBr	
8.	Which one of the follows	ng is the most volatile acid?		21.		aCl, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> and conc. H <sub>2</sub> SO <sub>4</sub>	•••••
	(a) HF	☐ (b) HCl			is obtained.		
	(c) HBr	□ (d) HI			(a) chromic chloride	(b) chromyl chloride	
9.	The acid which cannot b	e kept in glass bottles is:			(c) chlorine	$\Box$ (d) none of these	
	(a) HI	□ (b) HBr		22.	-	the Deacon's process for	the
	(c) HF	☐ (d) HCl			manufacture of chlorine		
10.	Which one of the follow	ing is the strongest acid?			(a) Cu	☐ (b) An alloy of copper	
	(a) HClO	☐ (b) HClO <sub>2</sub>			(c) CuCl <sub>2</sub>	□ (d) CuS	
	(c) HClO <sub>3</sub>	☐ (d) HClO <sub>4</sub>		23.	Which one of the follow	ving acts as an antichlor?	
11.	Which one of the following	ng is the strongest oxidising ag	ent?		(a) MnO <sub>2</sub>	$\Box$ (b) Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	
	(a) HClO	☐ (b) HClO <sub>2</sub>		ş	(c) $K_2Cr_2O_7$	☐ (d) Na <sub>2</sub> SO <sub>4</sub>	
	(c) HClO <sub>3</sub>	☐ (d) HClO <sub>4</sub>		24.	One gas bleaches the c	colour of flowers by reduction	n and
12.	Consider the following of	xides:			other by oxidation. The	se gases are:	
	1. OF <sub>2</sub> 2. Cl <sub>2</sub> O 3. Br <sub>2</sub> O	)			(a) SO <sub>2</sub> and Cl <sub>2</sub>	☐ (b) CO and Cl <sub>2</sub>	
	The correct sequence of	X—O—X bond angle is:			(c) NH <sub>3</sub> and SO <sub>2</sub>	(d) H <sub>2</sub> S and Br <sub>2</sub>	
	(a) $1 > 2 > 3$	$\Box$ (b) 3 > 2 > 1		25.	Bromine occurs as a bro		
	(c) $2 > 1 > 3$	$\Box$ (d) 1 > 3 > 2			(a) nitre	☐ (b) tincal	
	[Hint: O	o: •o•	]		(c) common salt	☐ (d) carnallite	
	1100	1050		26.	Bromine is prepared in t		
	Br Br	Cl Cl F	F		(a) by heating KBr with	•	
13.	Which one of the follow	ing has hydrogen bonding?			•	$MnO_2$ with conc. $H_2SO_4$	
	(a) HI	☐ (b) HBr			(c) by heating KBr with	_	
	(c) HF	☐ (d) HCl				ars through KBr solution	
				1	(a) by passing 12 vapou	us amongu voi sommon	

27.	Caliche is:	40.	A substance $X$ when heated with conc. $H_2SO_4$ liberates	a
	(a) impure nitre $\Box$ (b) impure carnallite $\Box$		gas which turns starch paper blue. The substance $X$ is:	
	(c) crude saltpetre $\Box$ (d) ashes of sea-weeds $\Box$		(a) NaI	
28.	Iodine is manufactured from:		(c) NaCl	
	(a) sea-weeds $\Box$ (b) carnallite $\Box$	41.	The chemical name of bleaching powder is:	
	(c) nitre $\Box$ (d) pure sodium iodide $\Box$		- 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1	
29.	Iodine displaces chlorine from which one of the compounds:	Ì	(b) calcium chlorohypochlorite	
	(a) KCl		• •	
	(c) $CCl_4$			
30.	Elements of which one of the following groups will form	42.	Identify the correct statements:	
	anions most readily?		1. On heating Rb(ICl <sub>2</sub> ) will decompose giving RbCl and IC	Č1.
	(a) Oxygen group $\Box$ (b) Nitrogen group $\Box$		2. CsI <sub>3</sub> will ionise to give Cs <sup>+</sup> and $I_3^-$ .	
	(c) Halogens		3. KBrICl will give KCl and IBr on heating.	
31	Which statement is correct about halogen?		4. In the reaction $I^- + I_2 \longrightarrow I_3^-$ , the Lewis acid is $I_2$ .	
<i>J</i> 1.	(a) They are all diatomic and form univalent ions			
	(b) They are all capable of exhibiting several oxidation states			
	(b) They are an eapable of exhibiting several oxidation states		[Hint: $CsI_3 \longrightarrow Cs^+ + I^- + I_2$ ]	
		43	Oxidising action increases in the following order:	
				-=
22	(-) 2)	1		
32.	Fluorine is the best oxidising agent because:	1 44	Fluorine does not show positive oxidation state because	
	(a) it has the highest electron affinity	TT.	-	
	(b) it has the highest electronegativity		• •	
	(c) it has the highest $E_{ox}^{o}$	1	` ,	
22	(d) it has the highest $E_{red}^{o}$		``	
33.	Iodine vapours are violet in colour because:	15	(2) 15 1110 110 11 01011111	
	(a) the molecules of iodine in vapour phase absorb green	43.	Available chlorine is liberated from bleaching powder who	
	and yellow radiations		(a) it is heated	
	(b) the molecules of iodine absorb red and violet radiations			
	and then emit them		(-)	
2.4	(c) it is a solid	1	(d) it is reacted with water	
34.	Among the elements of group 17, fluorine is the most reactive	46.	Bromine can be liberated from potassium bromide soluti	on
	owing to its:		by the action of:	_
	(a) electronegativity			
	(b) small size		( ) 1	
	(c) extremely high oxidising power and low dissociation	47.	Which of the following is not oxidised by MnO <sub>2</sub> ?	
	energy of F—F bond			
	(d) all the above factors are responsible for high reactivity	ļ	(c) $Br^ \Box$ (d) $I^-$	
~~	of fluorine		[Hint: The fluoride ion: F: is extremely stable. Hence, it is	not
35.	Which one of the following reacts with chlorine to form		oxidised by chemical reagents.]	
	phosgene?	48.	Bleaching properties of bleaching powder are due to its:	
	(a) $SO_2$	10.		_
26	(c) NO			H
36.	Which of the following elements does not show positive	1. 40	(c) basic properties	
	oxidation state?	49.	Which one of the following halogens is purified	bу
	(a) Fluorine		sublimation?	_
	(c) Oxygen $\square$ (d) Sulphur $\square$	}	(a) F	
37.	Slaked lime reacts with chlorine to form:		(c) Br	
	(a) $Ca(OCl)_2$ $\Box$ (b) $Ca(OCl)Cl$ $\Box$	50.	In a given sample of bleaching powder, the percentage	
	(c) $Ca(ClO_3)_2$ $\Box$ (d) $CaCl_2$ $\Box$		available chlorine is 49. The volume of chlorine obtained	l if
38.	Iodine is liberated from KI solution when treated with:		10 g of the sample is treated with HCl at N.T.P. is:	_
	(a) $ZnSO_4$ $\Box$ (b) $CuSO_4$ $\Box$		(a) 1.5 litre	
	(c) $NiSO_4$ $\Box$ (d) $FeSO_4$ $\Box$		(c) 15.0 litre	
39.	Iodine may be liberated from sodium iodate by reacting with:	51.	Conc. H <sub>2</sub> SO <sub>4</sub> is not used to prepare HBr from KBr because	
-	(a) $H_2SO_4$ $\Box$ (b) $NaHSO_3$ $\Box$		(a) reacts too slowly with KBr	
	(c) $\overline{\text{KMnO}_4}$ $\square$ (d) $\overline{\text{HCl}}$ $\square$		(b) reduces HBr	
	- · · · · · · · · · · · · · · · · · · ·			

		.494	and the state of t	
	(c) oxidises HBr	1	(a) fluorine	
	(d) oxidises KBr to KBrO <sub>3</sub> $\Box$		(c) bromine $\Box$ (d) iodine	
52.	Which one of the following is the strongest acid?	66.	When I2 is passed through solutions of KCl, KF and I	KBr
	(a) $SO(OH)_2$ $\Box$ (b) $SO_2(OH)_2$ $\Box$		respectively: [C.E.E.T. (Haryana) 20	000]
	(c) $CIO_2(OH)$ $\Box$ (d) $CIO_3(OH)$ $\Box$		(a) Cl <sub>2</sub> and Br <sub>2</sub> are evolved	
53.	Which of the following is the anhydride of perchloric acid?		(b) Cl <sub>2</sub> is evolved	
	(a) $Cl_2O$ $\Box$ (b) $ClO_2$ $\Box$	1.	(c) Cl <sub>2</sub> , Br <sub>2</sub> and F <sub>2</sub> are evolved	
٠.	$\Box$ (c) $\Box$ $\Box$ (d) $\Box$ $\Box$		(d) none of the above	
54.	HBr and HI can reduce H <sub>2</sub> SO <sub>4</sub> , HCl can reduce KMnO <sub>4</sub> and	67.	Iodine deficiency in diet is known to cause:	
*	HF can reduce:		(a) beri-beri	
	(a) $K_2Cr_2O_7$		(c) rickets	
	(c) $H_2SO_4$ $\square$ (d) none of these $\square$	68.	Chlorine is mixed with drinking water so that:	
55.	Chlorine acts as a bleaching agent only in the presence of:	00.	(a) bacteria are killed $\Box$ (b) dirt is removed	
	(a) dry air		•	
	(c) moisture $\Box$ (d) pure oxygen $\Box$	60	**	
56.	Which of the following pairs is not correctly matched?	69.	Which of the following has the greatest reducing power	
	(a) A halogen which is liquid at room temperature—Bromine	•	(a) HBr	
		70	(c) HCl	
•	(b) The most electronegative element—Fluorine □	/0	Concentrated HNO <sub>3</sub> reacts with iodine to give:	
	(c) The most reactive halogen—Fluorine		(a) HI	
	(d) The strongest oxidising agent— <i>lodine</i>		(c) $HOIO_2$	
57.	Which of the following statements is correct for CsBr <sub>3</sub> ?	71.	The correct order of increasing bond angles in the follow	ving
	(a) It is a covalent compound		species is :	
	(b) It contains Cs³+ and Br⁻ ions □		(a) $Cl_2O < ClO_2 < ClO_2^ \square$ (b) $ClO_2 < Cl_2O < ClO_2^-$	
	(c) It contains Cs <sup>+</sup> and Br <sub>3</sub> ions		(c) $Cl_2O < ClO_2^- < ClO_2$ $\Box$ (d) $ClO_2^- < Cl_2O < ClO_2$	
	(d) It contains $Cs^+$ , $Br^-$ and lattice $Br_2$ molecule	72.	Which of the following is not a pseudohalide ion?	
58.	Which of the following is most stable towards heat?		(a) SCN <sup>-</sup>	
	(a) HCl		(c) $ICl_2^-$	
	(c) HBr	73.	The following acids have been arranged in order	of
59.	The silver halide, which is least soluble in NH <sub>4</sub> OH is:		decreasing acid strength. Identify the correct order:	
	(a) AgF		ClOH(I) BrOH(II) IOH(III)	
	(c) $AgBr$ $\Box$ (d) $AgI$ $\Box$		(a) $I > II > III$	
60.	Fluorine reacts with water to give:		(c) $III > II > I$ $\Box$ (d) $I > III > II$	
	(a) hydrogen fluoride and oxygen □	74.	The acid employed for etching of glass is:	
	(b) hydrogen fluoride and ozone		(a) $H_2SO_4$ $\Box$ (b) $HClO_4$	
	(c) hydrogen fluoride and oxygen fluoride		(c) HF	
	(d) hydrogen fluoride, oxygen and ozone	75.	Hydrogen fluoride is a liquid unlike other hydrogen hali	
61.	When bleaching powder is treated with carbon dioxide:		because:	<b>u</b> 00,
	(a) chlorine is evolved		(a) H—F bond is strong	
	(b) calcium chloride is formed $\Box$		(b) F-atom is small in size	
	(c) no reaction occurs	-	(c) Hydrogen bonding is present	
	(d) it absorbs the gas		(d) HF is a weak acid	
62.	Bleaching powder is an example of:	76		
	(a) an acidic salt	/0.	Hydrogen bromide is dried by passing the gas through	
	(c) a double salt $\Box$ (d) a mixed salt $\Box$		(a) quick lime	
63.	The outermost electronic configuration of the most electro-		(b) anhydrous calcium chloride	
	negative element is:		(c) potassium hydroxide pellets	
	(a) $ns^2np^3$ $\Box$ (b) $ns^2np^4$ $\Box$		(d) conc. H <sub>2</sub> SO <sub>4</sub>	
	(c) $ns^2np^5$ $\Box$ (d) $ns^2np^6$ $\Box$	77.		
64.	Among the halogens, the one which is oxidised by nitric acid	1	(a) fluorine	
	is: [C.E.E.T. (Haryana) 2005]		(c) chlorine	
	(a) fluorine $\Box$ (b) chlorine $\Box$	78.	3	
	(c) bromine $\Box$ (d) iodine $\Box$		(a) $ClO_4^-$	
65.			(c) ICl and $O_3$ $\square$ (d) $IO_3^-$ and $Cl_2$	
	besides zero:		[Hint: $ClO_3 + I_2 \longrightarrow 2lO_2 + Cl_2$ ]	

79.	Which of the following is a preparation of chlorine?	92.	The structure of IF <sub>7</sub> is:	
	(a) HCl acting on KMnO <sub>4</sub> $\square$ (b) HCl acting on Na <sub>2</sub> O <sub>2</sub> $\square$		(a) trigonal bipyramid	
	(c) Electrolysis of brine $\Box$ (d) All of these $\Box$		(c) pentagonal bipyramid   (d) tetrahedral	
80.	The shape of $O_2F_2$ is similar to : [A.I.I.M.S. 2004]	93.	Which of the following is the strongest acid?	
	(a) $H_2O_2$ $\square$ (b) $C_2F_2$ $\square$		(a) HBr	
	(c) $H_2F_2$ $\square$ (d) $C_2H_2$ $\square$		(c) $H_2S$	
81.	Bleaching powder is obtained by the interaction of chlorine	94.	Which of the following has the highest value of dip	ole
	and:		moment?	
	(a) dilute solution of $Ca(OH)_2$		(a) HCl (b) HF	
	(b) concentrated solution of $Ca(OH)_2$		(c) HI	
	(c) dry calcium oxide $\Box$ (d) dry slaked lime $\Box$	95.	A radioactive halogen is:	
82.	Which amongst the following reactions cannot be used for		(a) polonium	-
	the respective preparation?		(c) astatine	
	(a) $2KBr + H_2SO_4$ (conc.) $\longrightarrow K_2SO_4 + 2HBr$	- 96.	Which of the following compounds contains both chlor	rine
	(b) NaCl + $H_2SO_4$ (conc.) $\longrightarrow$ NaHSO <sub>4</sub> + HCl		and fluorine?	
	(c) $NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$		(a) teflon	
	(d) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$		(c) freon	
02		97.	Which is formed when K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , CaCl <sub>2</sub> and conc. H <sub>2</sub> SO <sub>4</sub>	are
83.	Which of the following possesses the highest bond energy?	:	heated?	
	(a) $F_2$		(a) $Cr_2(SO_4)_3$ $\square$ (b) $CrCl_3$	
D/I	- (-) -2		(c) $CrO_2Cl_2$ $\square$ (d) $K_2CrO_4$	
84.	Astatine is the element below iodine in the group VIIA of	98.	Chlorine water on cooling deposits greenish-yellow crys	tals
	the periodic table. Which of the following statements is not		of:	
	true for astatine?		(a) $Cl_2 \cdot 2H_2O$ $\Box$ (b) $Cl_2 \cdot H_2O$	
	(a) It is less electronegative than iodine		(c) Cl <sub>2</sub> ·3H <sub>2</sub> O	
	(b) It will exhibit only -1 oxidation state	99.	A white deposit forms over the bottles containing conc. I	HC1
	(c) Intermolecular forces between the astatine molecules will		when kept for a long time in the laboratory. The wl	
	be larger than between iodine molecules  (d) It is composed of diatomic molecules		deposit is due to the formation of:	
05	(-)		(a) ammonium chloride	
85.	Order of boiling point is: [D.P.M.T. 2005]		(c) sodium carbonate	
	(a) HF > HI > HBr > HCl □ (b) HF > HBr > HI > HCl □	100.	Dry Cl <sub>2</sub> reacts with dry SO <sub>2</sub> to form:	
			(a) thionyl chloride	
	(-)		(c) sulphur dichloride	e□
04		101.		
86.	Halogens exist in $-1$ , $+1$ , $+3$ , $+5$ and $+7$ oxidation states.		(a) dry conditions $\square$ (b) presence of HCl only	
	The halogen that exists only in -1 oxidation state is:		(c) moist conditions	
	[P.E.T. (Kerala) 2010] (a) I	102.	Which of the following statements is correct?	
			[B.H.U. 19	997]
07			(a) All halogens form oxyacids	
87.			(b) Only chlorine and bromine form oxyacids	
	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \		(c) All halogens except fluorine form oxyacids	
00	( ) #		(d) Only iodine forms oxyacid	
88.	Which of the following polyhalides is not known?	103.	Which of the following statements is not correct whe	en a
	(a) $Cl_3$		mixture of NaCl and K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> is gently warmed with co	
90	( ) 3		$H_2SO_4$ ?	
89.	The iodine atom in $ICl_2^-$ involves: (a) $sp_3^3d$ hybridization $\square$ (b) $sp_3^3d^2$ hybridization $\square$		(a) A deep red vapour is evolved	
	(a) $sp^3d$ hybridization $\square$ (b) $sp^3d^2$ hybridization $\square$ (c) $sp^2$ hybridization $\square$ (d) $sp^3$ hybridization $\square$		(b) The vapour when passed into NaOH solution give	es a
00	When the vapours of chromyl chloride are passed through		yellow solution of Na <sub>2</sub> CrO <sub>4</sub>	
90.	· · · · · · · · · · · · · · · · · · ·		(c) Chlorine gas is evolved	
	NaOH solution, it turns yellow. This is due to formation of:		(d) Chromyl chloride is formed	
	(a) $Na_2Cr_2O_7$	104.		
Ω1	(c) CrO <sub>3</sub>		3NaClO Heat NaClO <sub>3</sub> + 2NaCl	
91.	2		(a) It is a disproportionation reaction	
	(a) pentagonal bipyramid (b) trigonal bipyramid (c) entabodies (d) tetrahedral		(b) Oxidation number of chlorine decreases as well	_
	(c) octahedral $\Box$ (d) tetrahedral $\Box$		increases in this reaction	

	(c) This reaction is used for the manufacture of halates E	]	(a) $Na_2S_4O_6$	
	(d) All of the above	]	(c) NaCl	
105.	On heating KClO <sub>3</sub> we get: [C.P.M.T. 1999	]	[Hint: $Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$ ]	
	(a) $KClO_2 + O_2$	1112.	Shape and hybridisation of IF <sub>5</sub> respectively are:	
	(c) $KCl + O_3$	]	[J.E.E. (Orissa) 200	08]
106.	The correct order of thermal stability of hydrogen halide	s	(a) trigonal bipyramidal, $sp^3d$	
	(H-X) is: [A.I.E.E.E. 2005]	1	. 2	
	(a) HI>HBr>HCl>HF  (b) HF>HCl>HBr>HI	- 1	(c) square pyramidal, $sp^3d^2$	
	(c) $HCl > HF > HBr > HI \square$ (d) $HI > HCl > HF > HBr \square$		(d) pentagonal pyramidal, $sp^3d^3$	
107.	The set with correct order of acidity is: [LJ.T. (S) 2001			
107.	C.B.S.E. 2007	110.	$Na_2S_2O_3$ is reduced by $I_2$ to: [J.E.E. (Orissa) 200	
	(a) HClO < HClO <sub>2</sub> < HClO <sub>3</sub> < HClO <sub>4</sub>	<u>.</u>	(a) $Na_2S$ $\square$ (b) $Na_2SO_4$	
	(b) $HClO_4 < HClO_3 < HClO_2 < HClO$	- }	(5) 11425458	
	(c) $HClO_4 < HClO_3 < HClO_2 < HClO_2$ (c) $HClO_4 < HClO_3 < HClO_2$	1 1 1 21	The oxidation states of iodine in HIO <sub>4</sub> , H <sub>3</sub> IO <sub>5</sub> and H <sub>5</sub> IO <sub>5</sub>	$O_6$
	(-)	_	are respectively: [A.I.I.M.S. 200	08]
100	(4) 110104 (110103 (11010	-	(a) $+1, +3, +7$	
108.	The reaction,		(c) $+7, +7, +7$ $\square$ (d) $+7, +5, +3$	
	$3ClO^{-}(aq.) \longrightarrow ClO_{3}^{-}(aq.) + 2Cl^{-}(aq.)$	115.	The electron affinity values (in kJ mol <sup>-1</sup> ) of three haloge	ens
	is an example of: [I.I.T. (S) 2001	]	X, Y and Z are respectively -349, -333 and -325. X, Y and	
	(a) oxidation reaction $\Box$ (b) reduction reaction $\Box$		respectively are: [D.C.E. (Engg.) 200	
	(c) disproportionation	1	(a) $F_2$ , $Cl_2$ , $Br_2$	$\Box$ .
	(d) decomposition reaction	]	(c) $Cl_2$ , $Br_2$ , $F_2$	
109.	Hydrogen bond is strongest in: [B.V. (Pune) 2002	]   116	Which one of the following reactions does not occur?	
	(a) F—H—O	]   110.		 AO1
	(c) F—H—F	]	[E.A.M.C.E.T. (Engg.) 200	
110.	Which of the following has highest bond strength?		(a) $F_2 + 2Cl^- \longrightarrow 2F^- + Cl_2$	
	[C.E.E. (Bihar) 2002	:]	(b) $Cl_2 + 2F^- \longrightarrow 2Cl^- + F_2$	
	(a) HI	ן כ	(c) $Br_2 + 2\Gamma \longrightarrow 2Br^- + I_2$	
		1	AN CHARLES ACHE IN	
	(c) HF ☐ (d) HBr l	]	(d) $Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$	
111.	(0) 111	-	(d) $Cl_2 + 2Br \longrightarrow 2Cl + Br_2$	Ц
111.	(c) HF $\square$ (d) HBr $\square$ Aqueous solution of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> on reaction with Cl <sub>2</sub> gives [1.1.T. 2008]	:	(d) $Cl_2 + 2Br \longrightarrow 2Cl + Br_2$	
	Aqueous solution of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> on reaction with Cl <sub>2</sub> gives			ш
Set	Aqueous solution of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> on reaction with Cl <sub>2</sub> gives [1.1.T. 2008]  II: This set contains questions with two or more contains	orrect and	swers.	
Set	Aqueous solution of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> on reaction with Cl <sub>2</sub> gives [1.1.T. 2008]  II: This set contains questions with two or more companies with the following halogens turn(s) starch iodine paper.	orrect and	swers. (d) HClO <sub>4</sub> > HClO <sub>3</sub> > HClO <sub>2</sub> > HClO	
Set	Aqueous solution of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> on reaction with Cl <sub>2</sub> gives [I.I.T. 2008] II: This set contains questions with two or more companies with two or more companies with the following halogens turn(s) starch iodine paper blue?	orrect and	swers.  (d) HClO <sub>4</sub> > HClO <sub>3</sub> > HClO <sub>2</sub> > HClO  The halogens, which are not attacked by conc. HNO <sub>3</sub> , a	are:
Set	Aqueous solution of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> on reaction with Cl <sub>2</sub> gives  [I.I.T. 2008]  II: This set contains questions with two or more contains the following halogens turn(s) starch iodine papellue?  (a) Cl <sub>2</sub>	orrect and 124.	swers.  (d) $HClO_4 > HClO_3 > HClO_2 > HClO$ The halogens, which are not attacked by conc. $HNO_3$ , at (a) $F_2$ $\square$ (b) $Cl_2$	are:
<b>Set</b> 117.	Aqueous solution of $Na_2S_2O_3$ on reaction with $Cl_2$ gives  [1.1.T. 2008]  II: This set contains questions with two or more complete which of the following halogens turn(s) starch iodine papellule?  (a) $Cl_2$	orrect and 124.	swers.  (d) $HClO_4 > HClO_3 > HClO_2 > HClO$ The halogens, which are not attacked by conc. $HNO_3$ , at (a) $F_2$	are:
<b>Set</b> 117.	Aqueous solution of $Na_2S_2O_3$ on reaction with $Cl_2$ gives [1.1.T. 2008]  II: This set contains questions with two or more of Which of the following halogens turn(s) starch iodine papellue?  (a) $Cl_2$	orrect and 124.	Swers.  (d) $HClO_4 > HClO_3 > HClO_2 > HClO$ The halogens, which are not attacked by conc. $HNO_3$ , a  (a) $F_2$ $\square$ (b) $Cl_2$ (c) $Br_2$ $\square$ (d) $I_2$ Which of the following are pseudohalide ions?	are:
<b>Set</b> 117.	Aqueous solution of $Na_2S_2O_3$ on reaction with $Cl_2$ gives  [1.1.T. 2008]  II: This set contains questions with two or more complete.  Which of the following halogens turn(s) starch iodine papellue?  (a) $Cl_2$		swers.  (d) $HClO_4 > HClO_3 > HClO_2 > HClO$ The halogens, which are not attacked by conc. $HNO_3$ , at (a) $F_2$	are:
<b>Set</b> 2 117.	Aqueous solution of $Na_2S_2O_3$ on reaction with $Cl_2$ gives [1.1.T. 2008]  II: This set contains questions with two or more complete.  Which of the following halogens turn(s) starch iodine papellue?  (a) $Cl_2$		swers.  (d) $HClO_4 > HClO_3 > HClO_2 > HClO$ The halogens, which are not attacked by conc. $HNO_3$ , a  (a) $F_2$ $\Box$ (b) $Cl_2$ (c) $Br_2$ $\Box$ (d) $I_2$ Which of the following are pseudohalide ions?  (a) $CNO^ \Box$ (b) $OCN^-$ (c) $RCOO^ \Box$ (d) $N_3^-$	are:
<b>Set</b> 117.	Aqueous solution of $Na_2S_2O_3$ on reaction with $Cl_2$ gives [1.1.T. 2008]  II: This set contains questions with two or more of the following halogens turn(s) starch iodine papellue?  (a) $Cl_2$	Direct and	swers.  (d) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$ The halogens, which are not attacked by conc. $\text{HNO}_3$ , at (a) $\text{F}_2$	are:
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Set : 117. 118. 119. 120.	Aqueous solution of $Na_2S_2O_3$ on reaction with $Cl_2$ gives [1.1.T. 2008]  II: This set contains questions with two or more of the following halogens turn(s) starch iodine papellue?  (a) $Cl_2$		swers.  (d) $HClO_4 > HClO_3 > HClO_2 > HClO$ The halogens, which are not attacked by conc. $HNO_3$ , at (a) $F_2$	are:
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Ausu	vers =								
<b>1.</b> (b)	2. (c)	3. (a)	<b>4.</b> (d)	5. (a)	<b>6.</b> (d)	<b>7.</b> (b)	<b>8.</b> (b)	<b>9.</b> (c)	<b>10.</b> (d)
<b>11.</b> (a)	<b>12.</b> (b)	13.	<b>14.</b> (c)	15. (a)	<b>16.</b> (c)	<b>17.</b> (d)	<b>18.</b> (c)	<b>19.</b> (a)	<b>20.</b> (c)
<b>21.</b> (b)	<b>22.</b> (c)	13. (2) 23. (b)	<b>24.</b> (a)	<b>25.</b> (d)	<b>26.</b> (b)	<b>27.</b> (c)	<b>28.</b> (a)	<b>29.</b> (d)	<b>30.</b> (c)
<b>31.</b> (a)	<b>32.</b> (d)	<b>33.</b> (a)	<b>34.</b> (d)	<b>35.</b> (d)	<b>36.</b> (a)	<b>37.</b> (b)	<b>38.</b> (b)	<b>39.</b> (b)	<b>40.</b> (a)
<b>41.</b> (b)	<b>42.</b> (a)	<b>43.</b> (d)	<b>44.</b> (d)	<b>45.</b> (b)	<b>46.</b> (b)	<b>47.</b> (a)	<b>48.</b> (a)	<b>49.</b> (d)	<b>50.</b> (a)
<b>51.</b> (c)	<b>52.</b> (d)	<b>53.</b> (d)	<b>54.</b> (d)	<b>55.</b> (c)	<b>56.</b> (d)	<b>57.</b> (d)	<b>58.</b> (a)	<b>59.</b> (d)	<b>60.</b> (d)
<b>61.</b> (a)	<b>62.</b> (d)	<b>63.</b> (c)	<b>64.</b> (d)	<b>65.</b> (a)	<b>66.</b> (d)	<b>67.</b> (b)	<b>68.</b> (a)	<b>69.</b> (b)	<b>70.</b> (c)
<b>71.</b> (d)	<b>72.</b> (c)	<b>73.</b> (a)	<b>74.</b> (c)	<b>75.</b> (c)	<b>76.</b> (b)	<b>77.</b> (b)	<b>78.</b> (d)	<b>79.</b> (d)	<b>80.</b> (a)
<b>81.</b> (d)	<b>82.</b> (a)	<b>83.</b> (b)	<b>84.</b> (b)	<b>85.</b> (a)	<b>86.</b> (c)	<b>87.</b> (b)	<b>88.</b> (c)	<b>89.</b> (a)	<b>90.</b> (b)
— <b>91.</b> (b)	<b>92.</b> (c)	93. (a)	<b>94.</b> (b)	95. (c)	<b>96.</b> (e)	<b>97.</b> (c)	98. (d)	99. (a)	<b>100.</b> (b)
<b>101.</b> (c)	<b>102.</b> (c)	<b>103.</b> (c)	<b>104.</b> (d)	<b>105.</b> (b)	<b>106.</b> (b)	<b>107.</b> (a)	<b>108.</b> (c)	<b>109.</b> (c)	110. (c)
<b>111.</b> (b)	<b>112.</b> (c)	<b>113.</b> (d)	<b>114.</b> (c)	<b>115.</b> (b)	<b>116.</b> (b)	<b>117.</b> (a,b)	<b>118.</b> (c,d)	119. (a,c)	120. (c,d)
<b>121.</b> (a,b,c)	122. (a,b)	123, (a,b,d)	<b>124.</b> (a,b,c)	<b>125.</b> (a,b,d)	<b>126.</b> (b,c)	<b>127.</b> (a,d)			

## **Objective Questions for IIT ASPIRANTS**



- 1. A greenish yellow gas reacts with an alkali metal hydroxide to form a halate which can be used in fireworks and safety matches. The gas and the halate are:
  - (a)  $Br_2$ ,  $KBrO_3$
- (b) Cl<sub>2</sub>, KClO<sub>3</sub>
- (c) I<sub>2</sub>, NaIO<sub>3</sub>
- (d)  $I_2$ ,  $KIO_3$

[Hint: The halate used in fireworks and safety matches is KClO<sub>3</sub>. Thus, the gas is Cl<sub>2</sub>.

$$3Cl_2 + 6KOH \longrightarrow KClO_3 + 5KCl + 3H_2O$$
 ]  
Greenish vellow gas

- 2. When chlorine water is added to an aqueous solution of sodium iodide in the presence of chloroform, a violet colouration is obtained. On adding more of chlorine water and vigorous shaking, the violet colour disappears. This shows the conversion of . . . . . into . . . . .
  - (a)  $I_2$ ,  $HIO_3$
- (b)  $I_2$ , HI
- (c) HI, HIO3
- (d) I<sub>2</sub>, HIO

[Hint:

$$Cl_2 + 2NaI \longrightarrow 2NaCl + I_2$$

(Violet colouration in chloroform)

$$5Cl_2 + 6H_2O + I_2 \longrightarrow 2HIO_3 + 10HCl$$
 ]

3. For  $(A) + K_2CO_3 + air \xrightarrow{Heat} (B)$ 

$$(B) + \operatorname{Cl}_2 \longrightarrow (C) \operatorname{pink}$$

Which of the following is correct?

- (a) (A) is black, MnO<sub>2</sub>; (B) is blue, K<sub>2</sub>MnO<sub>4</sub> and (C) is pink, KMnO<sub>4</sub>
- (b) (A) is green,  $Cr_2O_3$ ; (B) is yellow,  $K_2CrO_4$  and (C) is pink,  $K_2Cr_2O_7$
- (c) (A) is black, MnO<sub>2</sub>; (B) is green, K<sub>2</sub>MnO<sub>4</sub> and (C) is pink, KMnO<sub>4</sub>
- (d) (A) is black, Bi<sub>2</sub>O<sub>3</sub>; (B) is colourless, KBiO<sub>2</sub> and (C) is pink, KBiO<sub>3</sub>

- $[ \mbox{Hint}: \begin{tabular}{ll} MnO_2 + K_2CO_3 + \frac{1}{2}O_2 & \longrightarrow K_2MnO_4 + CO_2 \\ & (Air) & (B) \\ & Green \\ \hline & 2K_2MnO_4 + Cl_2 & \longrightarrow 2KMnO_4 + 2KCl \end{tabular} ]$
- 4. Euchlorine is:
  - (a) obtained by heating perchlorate with conc. HCl
  - (b) a chloride of europium
  - (c) a mixture of Cl<sub>2</sub> and Cl<sub>2</sub>O<sub>7</sub>
  - (d) a mixture of Cl2 and ClO2

[Hint: When KClO<sub>3</sub> is heated with conc. HCl, a mixture of Cl<sub>2</sub> and ClO<sub>2</sub> is formed. This mixture is known as euchlorine.  $2\text{KClO}_3 + 4\text{HCl} \longrightarrow 2\text{KCl} + 2\text{ClO}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}]$ 

- 5. Which is incorrectly matched?
  - (a)  $CsBr_3 \rightleftharpoons Cs^+ + Br_3^- \rightleftharpoons Cs^+ + Br_2^- + Br_2$
  - (b)  $I_4O_9 \rightleftharpoons I^{3+} + 3(IO_3)^-$
  - (c)  $AgBrO_3 \rightleftharpoons Ag^+ + BrO_3^-$
  - (d)  $I_2O_4 \rightleftharpoons IO_2^+ + IO_2^-$

[Hint: 
$$I_2O_4 \rightleftharpoons I^+ + IO_4^-$$
]

- 6. A certain compound (X) when treated with copper sulphate solution yields a brown precipitate. On adding hypo solution, the precipitate turns white. The compound is:
  - (a) K<sub>2</sub>CO<sub>3</sub>
- (b) KI

(c) KBr

(d)  $K_3PO_4$ 

$$[\mbox{Hint}: \quad CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4 \, ; \\ 2CuI_2 \longrightarrow Cu_2I_2 + I_2 \, ; \\ \mbox{White} \quad \mbox{Brown} \label{eq:cuSO_4}$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$
 Colourless

7. The products of the chemical reaction between  $Na_2S_2O_3$ ,  $Cl_2$  and  $H_2O$  are :

(a) S, HCl, Na<sub>2</sub>SO<sub>4</sub>

(b) S, HCl, Na<sub>2</sub>S

(c) S, HCl, Na<sub>2</sub>SO<sub>3</sub>

(d) S, NaClO<sub>3</sub>

[Hint:  $Na_2S_2O_3 + H_2O + Cl_2 \longrightarrow Na_2SO_4 + S + 2HCl$ ]

**8.** Fluorine on reaction with  $KIO_3(aq.)$  gives (A) and on reaction with KHSO<sub>4</sub> gives (B). (A) and (B) are:

(a) KIO<sub>4</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

(c) HF,  $K_2S_2O_8$ 

(d)  $I_2, K_2S_2O_8$ 

[Hint:  $KIO_3 + F_2 + H_2O \longrightarrow KIO_4 + H_2F_2$ ;  $2KHSO_4 + F_2 \longrightarrow K_2S_2O_8 + 2HF$ 

9. KClO<sub>3</sub> on reaction with SO<sub>2</sub> gives (A) and on reaction with conc.  $H_2SO_4$  gives (B). (A) and (B) are:

(a) KCl, HClO<sub>4</sub>

(b) Cl<sub>2</sub>, ClO<sub>2</sub>

(c) KCl, HClO<sub>3</sub>

(d) Cl<sub>2</sub>, HClO<sub>4</sub>

[Hint:  $KClO_3 + 3SO_2 + 3H_2O \longrightarrow KCl + 3H_2SO_4$ 

 $3KClO_3 + 3H_2SO_4 \longrightarrow 3KHSO_4 + 3HClO_3$  $2HClO_3 \longrightarrow 2ClO_2 + H_2O + O$ 

 $HClO_3 + O \longrightarrow HClO_4$ 

 $3KClO_3 + 3H_2SO_4 \longrightarrow 3KHSO_4 + 2ClO_2 + HClO_4 + H_2O$ 

10.

$$\operatorname{Br}_2 + \operatorname{OH}^- \longrightarrow (A) + (B)$$

 $(A) + (B) + H^{+} \longrightarrow Br_2$ 

(A) gives yellow precipitate with AgNO<sub>3</sub>. (A) and (B) are:

(a) Br, BrO

(b)  $Br^-$ ,  $BrO_3^-$ 

(c) BrO, BrO3

(d)  $BrO^-$ ,  $BrO_4^-$ 

Hint:

$$3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O$$

$$5Br^{-} + BrO_{3}^{-} + 6H^{+} \longrightarrow 3Br_{2} + 3H_{2}O$$

11. 10 g of bleaching powder on reaction with KI required 50 mL of 2N hypo solution. Thus, % of bleaching powder is:

(a) 100

(b) 80

(c) 63.5

(d) 35.5

[Hint: 50 mL 2N hypo soln.  $\equiv$  50 mL 2N I<sub>2</sub> soln.  $\equiv$  50 mL 2N Cl<sub>2</sub> soln.  $\equiv$  50 mL 2N CaOCl<sub>2</sub> soln.

 $\equiv$  6.35 g CaOCl<sub>2</sub>

 $\%\frac{6.35}{10} \times 100 = 63.5$ ]

12.  $HClO_4 + P_2O_5 \longrightarrow (A) + (B)$ 

(A) and (B) are:

(a) HClO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>

(b) Cl<sub>2</sub>O<sub>6</sub>, HPO<sub>3</sub>

(c) ClO<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>

(d) Cl<sub>2</sub>O<sub>7</sub>, HPO<sub>3</sub>

[Hint:  $2HClO_4 + P_2O_5 \longrightarrow Cl_2O_7 + 2HPO_3$ ]

13.  $AgClO_3 + (A) \longrightarrow (B) + (C) + (D)$ 

The substances (A), (B), (C) and (D) are:

(a)  $Cl_2$ , AgCl,  $ClO_2$ ,  $O_2$ 

(b)  $Cl_2$ , Ag,  $Cl_2O_6$ ,  $O_2$ 

(c) H<sub>2</sub>, AgCl, H<sub>2</sub>O, O<sub>2</sub>

(d) HClO, AgCl, Cl<sub>2</sub>O, O<sub>2</sub>

[Hint:  $2AgClO_3 + Cl_2 \longrightarrow 2AgCl + 2ClO_2 + O_2$ ]

14. Select the correct statement(s):

(a) Cl<sub>2</sub>O and ClO<sub>2</sub> are used as bleaching agents and as germicides

(b) ClO<sub>2</sub> is the anhydride of HClO<sub>2</sub> and HClO<sub>3</sub>

(c) I<sub>2</sub>O<sub>5</sub> is used in the quantitative estimation of CO

(d) All of the above are correct

[Hint:  $2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$  $I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$ 

15. Which one of the following represents the reaction between fluorine and cold NaOH (dil.)?

(a)  $2F_2 + 4NaOH \longrightarrow 4NaF + 2H_2O + O_2$ 

(b)  $3F_2 + 6NaOH \longrightarrow 5NaF + NaFO_3 + 3H_2O$ (c)  $F_2 + 2NaOH \longrightarrow NaF + NaOF + H_2O$ 

(d)  $2F_2 + 2NaOH \longrightarrow 2NaF + OF_2 + H_2O$ 

16. Which one of the following pairs of reactants does not form oxygen when they react with each other?

(a) F<sub>2</sub>, NaOH solution (hot, conc.)

(b)  $F_2, H_2O$ 

(c) Cl<sub>2</sub>, NaOH solution (cold, dilute)

(d) CaOCl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> (dilute, small amount)

[Hint: (a)  $2F_2 + 4NaOH \longrightarrow 4NaF + 2H_2O + O_2$ (Hot, conc.)

(b)  $2F_2 + 2H_2O \longrightarrow 4HF + O_2$ 

Cl<sub>2</sub> + 2NaOH ---→ NaCl + NaClO + H<sub>2</sub>O (c)

 $2CaOCl_2 + H_2SO_4 \longrightarrow CaCl_2 + CaSO_4 + 2HCl + O_2$ (d)

<del>l</del>uswers

1. (b)

2. (a)

3. (c)

5, (d)

**6.** (b)

7. (a)

Σ.

**8.** (c)

9. (a)

10. (b)

11. (c)

12. (d)

# **Assertion-Reason Type Questions**

The following questions consist of two statements each, printed as Assertion (A) and Reason (R). While answering these questions, you are required to choose any one of the following responses:

- (a) If both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) If (A) is true but (R) is false.
- (d) If (A) is false but (R) is true.
- (e) If both the (A) and (R) are false.
- 1. (A) HClO<sub>4</sub> is a stronger acid than HClO<sub>3</sub>.
  - (R) Oxidation state of chlorine in HClO<sub>4</sub> is +7 and in HClO<sub>3</sub>; it is +5.
- 2. (A) The bond between F-F is stronger than between CI-CI.
  - (R) Atomic size of F is smaller than that of Cl.
- 3. (A) Iodine displaces chlorine from KClO<sub>3</sub>.
  - (R) Iodine is stronger oxidising agent than chlorine.

- 4. (A) All the halogens are coloured.
  - (R) Halogen molecules absorb some wavelengths of visible light and the electrons are promoted to higher energy molecular orbitals.
- 5. (A) Fluorine does not show oxidation number greater than zero.
  - (R) The halogens chlorine, bromine and iodine can show positive oxidation states of +1, +3, +5 and +7.
- 6. (A) The boiling point of HF is maximum among the hydracids of halogens.
  - (R) The high boiling point of HF is due to H-bonding on account of high electronegativity of fluorine.
- 7. (A) Fluorine forms a salt of an oxyacid when treated with NaOH solution.
  - (R) Fluorine can be prepared by passing chlorine through sodium fluoride solution.
- 8. (A) Halogens do not directly combine with oxygen. However, oxides are obtained indirectly.
  - (R) The oxides of fluorine form oxyacids with water.

1. (b)

2. (d)

3. (c)

4. (a)

5. (b)

**6.** (a)

7. (e)

value is due to:

its formation

(d) all of the above

chlorine in the sample is:

[**Hint**: CaOCl<sub>2</sub>·H<sub>2</sub>O  $\longrightarrow$  Cl<sub>2</sub>  ${}^{145}$   ${}^{71}$   ${}^{1}$   ${}^{1}$   ${}^{1}$   ${}^{1}$ 

8. (c)

The percentage of available chlorine in commercial samples

of bleaching powder is usually between 33-38%. The low

(a) incomplete reaction between slaked lime and Cl<sub>2</sub> during

(c) decomposition of bleaching powder when kept in air

3. 3.55 g of bleaching powder when treated with acetic acid and

excess of KI liberated iodine which required 60 mL of 0.5 N

sodium thiosulphate solution. The percentage of available

(b) impurities present in the original slaked lime

## QUESTIONS THOUGH



#### THOUGHT 1

Bleaching powder is a mixed salt of hydrochloric acid and hypochlorous acid. It has the formula, CaOCl<sub>2</sub>·H<sub>2</sub>O. It is manufactured by the action of chlorine on dry slaked lime at 40°C. There is also a view that bleaching powder is a mixture of calcium hypochlorite and basic calcium chloride [Ca(OCl)<sub>2</sub> + CaCl<sub>2</sub>·Ca(OH)<sub>2</sub>·H<sub>2</sub>O].

The amount of chlorine obtained from a sample of bleaching powder by the treatment with excess of dilute acids or CO2 is called available chlorine. A good sample of bleaching powder contains 35-38% of available chlorine. On long standing, it undergoes auto-oxidation and the amount of available chlorine decreases.

The estimation of available chlorine is done volumetrically by (a) iodometric method or by (b) arsenite method.

In textile industry, the cotton cloth is mainly bleached with the help of bleaching powder.

- 1. Maximum percentage of available chlorine on the basis of CaOCl<sub>2</sub>·H<sub>2</sub>O formula is: (a) 35 · · · · · · (b) 40
  - (c) 45

- (d) 49

(a) 30.0

(b) 25.0

(c) 20.0

(d) 35.0

[**Hint**: 60 mL 0.5 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln.  $\equiv$  60 mL 0.5 N I<sub>2</sub> soln.  $\equiv$  60 mL 0.5 N Cl<sub>2</sub> soln.

% available 
$$Cl_2 = \frac{60 \times 0.5 \times 35.5}{1000 \times 3.55} \times 100 = 30$$
 ]

- **4.** On long standing, the bleaching powder undergoes auto-oxidation. The products formed are :
  - (a) calcium chloride only
  - (b) calcium chlorate only
  - (c) calcium chloride and calcium chlorate
  - (d) calcium chloride and calcium chlorite

[Hint:  $6CaOCl_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2$ ]

- 5. The chemical name of bleaching powder is:
  - (a) calcium hypochlorite
  - (b) calcium chlorohypochlorite
  - (c) calcium chlorate
  - (d) calcium perchlorate

## THOUGHT 2

A salt (A) when heated with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and conc. H<sub>2</sub>SO<sub>4</sub> liberates a gas which is absorbed in NaOH solution. The NaOH solution turns yellow. When this solution is acidified with acetic acid and lead acetate solution is added, a yellow precipitate (B) is formed,

(A) is mixed with  $MnO_2$  and heated with conc.  $H_2SO_4$  when a gas (C) is evolved which turns starch-iodide paper blue.

- 1. The acidic radical present in the salt (A) is:
  - (a)  $NO_3$

(b) Cl

(c)  $S^{2-}$ 

- (d) I
- The compound formed, which turns NaOH solution yellow, is:
  - (a) Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
- (b) Na<sub>2</sub>S

(c) NaI

- (d) Na<sub>2</sub>CrO<sub>4</sub>
- 3. What is the colour of gas which is evolved when salt (A) is heated with  $MnO_2$  and  $H_2SO_4$ ?
  - (a) violet
- (b) brown
- (c) greenish yellow
- (d) colourless

# THOUGHT 3

Halogens react with each other to form a number of compounds called interhalogen compounds. Their general formula is  $AX_n$ ; where A is less electronegative halogen while X is a more electronegative halogen and n is its number. The interhalogen compounds are essentially covalent and more reactive than the halogens since the bond A—X is weaker than A—A or X—X bond. The reactions of interhalogens are similar to those of halogens.

1. Which of the following interhalogen compounds is not possible?

(a) IF<sub>7</sub>

(b) IF<sub>5</sub>

(c) CIF<sub>3</sub>

- (d) FCl<sub>3</sub>
- 2. Which halogen shows maximum oxidation state in forming interhalogen compound ?
  - (a) I

(b) Br

(c) C1

- (d) F
- 3. How many lone pairs of electrons are present on chlorine in ClF<sub>3</sub> molecule?
  - (a) 0

(b) 1

(c) 2

- (d) 3
- 4. Which of the following statements is wrong for interhalogen?
  - (a) The value of n in  $AX_n$  (interhalogen) can be 1, 3, 5 or 7
  - (b) The value of n in  $AX_n$  (interhalogen) can be 2, 4, or 6
  - (c) A can never be fluorine as it is most electronegative halogen
  - (d) X can never be iodine as it is least electronegative halogen

## THOUGHT 4

Fluorine, the first member of group 17, differs from the other members of the group in many respects due to following reasons:

- (i) Its size is very small
- (ii) It has very high electronegativity
- (iii) It does not have vacant d-orbitals in the valence shell
- (iv) Its dissociation energy in the molecular form  $(X_2)$  is the least
- **1.** Which member of the group 17 does not show positive oxidation state?
  - (a) Iodine
- (b) Bromine
- (c) Chlorine
- (d) Fluorine
- 2. Which has the maximum molar enthalpy of vaporisation?
  - (a) HF

(b) HCl

(c) HBr

- (d) HI
- 3. Which of the following bonds is the strongest?
  - (a) F-F
- (b) Cl—Cl
- (c) Br—Br
- (d) I—I
- 4. Which halogen does not form any oxyacid?
  - (a) Iodine
- (b) Bromine
- (c) Chlorine
- (d) Fluorine
- 5. The most basic among the following is:
  - (a) CI

(b) Br

(c) F

(d) I

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Thought 1 1. (d) 2. (d) 3. (a) 4. (c) 5. (b)
Thought 2 1. (b) 2. (d) 3. (c)

**Thought 3 1.** (d) **2.** (a) **3.** (c) **4.** (b)

**Thought 4 1.** (d) 2. (a) 3. (b) 4. (d) 5. (c)

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. Sodium iodate is treated with calculated amount of sodium bisulphite to prepare iodine. How many moles of sodium bisulphite required to prepare one mole of iodine from sodium iodate?
- 2. In the molecule ICl<sub>3</sub>, how many lone pairs of electrons are associated with iodine?
- 3. In the known interhalogen compounds  $AB_n$ , what is maximum value of n?
- 4. In a given sample of bleaching powder, the percentage chlorine is 49. The volume in litres of chlorine obtained if 20g of the sample is treated with HCl at NTP is:
- 5. What is the oxidation state of iodine in  $H_5IO_6$ ?
- 6. How many orbitals are involved in the hybridisation of iodine in IF<sub>5</sub>?
- 7. Chlorine water on cooling deposits greenish yellow crystals of formula Cl<sub>2</sub>·XH<sub>2</sub>O. What is the value of X?

**2.** (2)  $sp^3d$  hyb.

- 1. (5)  $2\text{NaIO}_3 + 5\text{NaHSO}_3 \longrightarrow 3\text{NaHSO}_4 + 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{I}_2$
- **4.** (3) Vol. of  $Cl_2 = \frac{49}{100} \times 20 \times \frac{22.4}{71} \approx 3$  litre
- **5.** (7) 5 + x 12 = 0, x = + 7**6.** (6)  $sp^3d^2$  hybridisation.
- 7. (8)

**3.** (7)

Group 18 or Zero

2 He Helium 1s<sup>2</sup>
10 Ne Neon 2s<sup>2</sup>2p<sup>5</sup>
18 Ar Argon 3s<sup>2</sup>3p<sup>5</sup>
36 Kr Krypton 4s<sup>2</sup>4p<sup>5</sup>
54 Xe Xeon 5s<sup>2</sup>5p<sup>5</sup>
86 Rn

CHAPTER 13



# The Elements of 18 or Zero Group

(Inert Gases or Noble Gases)

## Contents:

- 13.1 Position in the Periodic Table
- 13.2 Occurrence

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- 13.3 History of the Discovery of Noble Gases
- 13.4 Isolation of Noble Gases from the Atmosphere
- 13.5 Separation of Noble Gases
- 13.6 Uses of Noble Gases
- 13.7 Compounds of Noble Gases
- 13.8 Importance of Noble Gases in Theoretical Chemistry
- 13.9 Determination of Atomic Mass of a Noble Gas

Group Period	VIIA (17)	Zero (18)
1	H (1)	He (2)
2	F (9)	Ne (10)
3	Cl (17)	Ar (18)
4	Br (35)	Kr (36)
5	I (53)	Xe (54)
6	At (85)	Rn (86)
7		Uuo (118)

## 13.1 POSITION IN THE PERIODIC TABLE

The zero or 18th group consists of seven elements; helium, neon, argon, krypton, xenon, radon and ununoctium. The zero group was unknown when **Mendeleev** presented the periodic table and has been inserted in the table only at a later stage. The existence of such a group may be naturally expected from the fact that there must be an inert group as transition when we go from highly electronegative elements (halogens) to highly electropositive elements (alkali metals). Thus, zero group occupies the intermediate position between the elements of VIIA (17th) and IA (1st) groups.

The members of zero group are the **end members** of respective periods of the periodic table. Helium is the end member of first period, neon the end member of second period, argon the end member of third period and so on. This is the only group of the periodic table, all members of which are gases and chemically inactive under ordinary conditions. On account of this, these are collectively called as **inactive gases or inert gases**. However, these are now called **noble gases** as some compounds of these gases have been obtained under certain specific conditions, *i.e.*, they do show some chemical activity under special conditions. They are also termed as **zerovalent elements** because they show zero valency due to chemical inertness. On account of zero valency, the group to which these elements belong is termed as zero group.

VIIA (Halogens) Electronegative elements	Zero group	IA (Alkali metals) Electropositive metals		
H (1)	He (2)	Li (3)		
F (9)	Ne (10)	Na (11)		
Cl (17)	Ar (18)	K (19)		
Br (35)	Kr (36)	Rb (37)		
I (53)	Xe (54)	Cs (55)		
At (85)	Rn (86)	Fr (87)		

Except last two members radon and ununoctium which are radioactive, all other members are present in atmosphere in very minute quantities. Thus, these are termed as rare gases of atmosphere.

The chemical inertness of these elements is due to the following reasons:

(i) Stable electronic configuration: All of these, except helium, have the highly stable  $s^2p^6$  configuration in the outer (valency) shell. Helium has the stable  $1s^2$  configuration.

On account of highly stable  $s^2p^6$  configuration in the valency shell, these elements have no tendency either to lose, gain or share electrons with the atoms of other elements, *i.e.*, their combining capacity or valency is zero. These elements are, thus, chemically inert.

- (ii) All the orbitals in the atoms of these elements are doubly occupied, *i.e.*, electrons are not available for sharing. Hence, these elements cannot form covalent compounds.
- (iii) The ionisation enthalpies of these elements are very high. Hence, the atoms of these elements have no tendency to lose electron from the outermost shell as to form cation.
- (iv) The electron gain enthalpy values of these elements are positive. Hence, the atoms of these elements have no tendency to accept electrons, *i.e.*, to form anions.

Element	At. No.	Electronic configuration	Configuration of outer-shell
Не	2	$\frac{1}{s^2}$	1s <sup>2</sup>
Ne	10	$1s^2$ , $2s^22p^6$	$2s^22p^6$
Ar	18	$-2, 8, 8$ $-1s^2, 2s^22p^6, 3s^23p^6$	$3s^23p^6$
Kr	36	2, 8, 18, 8 $1s^2$ , $2s^22p^6$ , $3s^23p^63d^{10}$ , $4s^24p^6$	$4s^24p^6$
Xe	54	2, 8, 18, 18, 8 $1s^2$ , $2s^22p^6$ , $3s^23p^63d^{10}$ , $4s^24p^64d^{10}$ , $5s^25p^6$	$5s^25p^6$
Rn	86	2, 8, 18, 32, 18, 8 $1s^2$ , $2s^22p^6$ , $3s^23p^63d^{10}$ , $4s^24p^64d^{10}4f^{14}$ , $5s^25p^65d^{10}$ , $6s^26p^6$	$6s^26p^6$
Uuo*	118	2, 8, 18, 32, 32, 18, 8 $1s^2$ , $2s^22p^6$ , $3s^23p^63d^{10}$ , $4s^24p^64d^{10}4f^{14}$ , $5s^25p^65d^{10}5f^{14}$ , $6s^26p^66d^{10}$ , $7s^27p^6$	$7s^27p^6$

Besides similar electronic configuration and chemical inertness, the following points justify the inclusion of these elements in the same group of the periodic table. A gradation in the properties is also observed with the increase of atomic number.

- (i) They are all colourless, odourless and tasteless gases.
- (ii) These gases do not burn and also do not help in burning.
- (iii) All are mono-atomic in nature as they have no combining

capacity. The specific heat ratio, *i.e.*,  $\frac{C_p}{C_v}$  for all the inert gases has been found to be 1.66 (theoretical value for mono-atomic character).

Mono-atomic character was also proved by bond order data, bond order of the molecules like He<sub>2</sub>, Ne<sub>2</sub> was calculated to be zero, *e.g.*,

He<sub>2</sub>: Four electron system; its molecular orbital configuration is

Bond order = 
$$\frac{1}{2}$$
 [Number of bonding electrons – Number of antibonding electrons]  
=  $\frac{1}{2}$  [2 - 2] = 0;

zero bond order proves mono-atomic character.

(iv) All have low values of **melting and boiling points.** These values increase gradually as the atomic number increases.

	-	•				
Element	He	Ne	Ar	, Kr	Xe	Rn
Melting point (K)	1	24.6	83.8	115.9	161.3	202
Boiling point (K)	4.2	27.1	87.2	119.7	165	211

Amongst the known elements, helium has got the lowest melting and boiling points. The low melting and boiling points of these gases are due to weak inter-molecular forces of attraction in these cases. The weak intermolecular forces, however, increase with increase of atomic mass from He to Rn and therefore, the melting and boiling points increase gradually.

(v) In a period of representative elements, it is observed that atomic radius decreases as the atomic number increases from 1st group to 17th group. However, the radii values of noble gases which come after the elements of group 17th are exceptionally high. This is due to the fact that in the case of noble gases, the atomic radii correspond to van der Waals' radii which are always larger than covalent radii. van der Waals' radii of noble gases increase gradually from He to Rn. This is due to addition of new energy shell from member to member.

(vi) All have high values of ionisation enthalpies. However, these values decrease from He to Rn. However, the ionisation enthalpy of the inert gas is highest amongst the members of the same period.

Element He Ne Ar Kr Xe Rn First ionisation 2372 2080 1520 1351 1170 1037 enthalpy 
$$(kJ \text{ mol}^{-1})$$

<sup>\*</sup>Recently discovered. It is synthetic, radioactive and unstable element. Not much is known about its properties.

- (vii) These gases are sparingly soluble in water (8 to 40 mL per litre at 25°C). The solubility, in general, increases with increasing atomic number.
- (viii) Except helium, these gases can be adsorbed by coconut charcoal at suitable temperatures.
- (ix) These gases give a characteristic spectra by which they can be easily identified.
- (x) These gases have fairly high electrical conductivity. They produce characteristic coloured lights when an electrical discharge is passed through them at low pressure.
- (xi) These gases are relatively difficult to be liquefied as very weak van der Waals' forces of attraction exist in these gases. However, the liquefaction becomes easier from He to Xe as forces increase gradually.

## 13.2 OCCURRENCE

The noble gases (except radon) always occur in the free state. The chief sources are:

1. Air: It is the most important source for the first five gases. They form about 1% by volume of the air. Argon is the principal constituent and others are present in minute quantities. The percentage by volume of various elements is as given:

Helium	$5.24 \times 10^{-4}$	Neon	$1.82 \times 10^{-3}$
Argon	$9.34 \times 10^{-1}$	Krypton	$1.45 \times 10^{-3}$
Xenon	$8.70 \times 10^{-6}$	_	

- **2. Natural gas:** The natural gas found in certain parts of America and Canada contains 2 to 7% helium. At present, most of the helium is obtained from this source.
- **3. Spring water:** The water of certain springs has been found to contain dissolved helium, argon and neon in very small amounts.
- **4. Radioactive minerals:** Radioactive minerals such as monazite, clevite, pitchblende and uranite contain considerable amounts of helium. The gas is produced as the result of radioactive disintegration of uranium and thorium present in the minerals but instead of escaping, it is retained by minerals probably in a state of solid solution. The gas is obtained when these minerals are either heated at 1000°C in vacuum or heated with sulphuric acid.

# 13.3 HISTORY OF THE DISCOVERY OF NOBLE GASES

The credit for the discovery of inert gases goes to William Ramsay and his co-workers.

## Discovery of argon

In 1785, the English chemist, Henry Cavendish performed an experiment by passing electric discharge through a mixture of purified air (dry) and excess of oxygen. Nitrogen was thus converted into corresponding oxides.

$$N_2 + O_2 \xrightarrow{\text{Electric}} 2NO$$
 $2NO + O_2 \longrightarrow 2NO_2$ 

The oxides of nitrogen and unused oxygen were removed by the use of caustic potash and alkaline pyrogallol solutions, respectively. Cavendish observed that a small volume of the gas which was about 1/120 part of the original air, was left. It was neither nitrogen nor oxygen. Cavendish, however, could not draw any conclusion regarding the nature of the residual gas. This experiment was not given any importance for about 109 years.

In the years 1893-94, Lord Rayleigh while working on accurate determination of densities of gases obtained nitrogen from two sources. The nitrogen obtained from the atmosphere was found to be heavier in comparison to the nitrogen obtained by heating a mixture of ammonium compound (NH<sub>4</sub>Cl) and sodium nitrite. The actual values were found to be 1.2572 g/L for atmospheric nitrogen and 1.2505 g/L for chemical nitrogen. Rayleigh repeated his experiments several times and each time he found the same difference. He, thus, concluded that the nitrogen, obtained from the atmosphere must contain some gas or gases which are heavier than nitrogen.

Rayleigh discussed the problem with Ramsay. Both took up the investigations to prove that a heavier gas was present in atmospheric nitrogen. Two methods were used for the preparation of the new gas:

(i) Ramsay method: This consisted of passing air over hot copper and heated magnesium to remove oxygen and nitrogen, respectively.

$$\begin{array}{c} \text{Air} \longrightarrow \text{heated copper} \longrightarrow \text{heated magnesium} \longrightarrow \text{residue} \\ 2\text{Cu} + \text{O}_2 \longrightarrow 2\text{CuO} \ ; \qquad 3\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2 \end{array}$$

The vapour density of the residue was determined and found to be 20.

(ii) Rayleigh method: Cavendish experiment was repeated. A mixture of air and oxygen was taken and an electric discharge of 6000-8000 volts was passed. After the removal of oxides of nitrogen and unreacted oxygen, the vapour density of the residual gas was determined and it also came to 20.

$$\begin{array}{c} N_2 + O_2 \longrightarrow 2NO \\ 2NO + O_2 \longrightarrow 2NO_2 \\ 2NO_2 + 2NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O \end{array}$$

Oxygen + Alk. pyrogallol ----- Oxygen absorbed

The gas was examined spectroscopically and the spectrum proved that this was an unknown gas. The gas was found to be chemically inert. The new gas was named argon (Greek: argos, lazy or inert). Later on, it was found that it was not a single gas but a mixture of many gases.

#### Discovery of Helium

On August 18, 1868, there occurred a total solar eclipse in

India. The sun's chromosphere was studied for the first time spectroscopically. **J.C. Jannsen** observed a new bright line in the yellow region of the sun's spectrum which did not coincide with the two known lines  $D_1$  and  $D_2$  due to sodium. He named the new line  $D_3$ . **Frankland and Lockyer** pointed out that new  $D_3$  line was due to a new element which did not occur on earth but only existed in the sun's chromosphere. They, therefore, named it **Helium** (Greek; *helios* means sun).

**Hillebrand,** in 1888, observed that a uranium mineral, clevite, on treatment with dilute sulphuric acid gave out a gas which he thought to be nitrogen as it was chemically inert. **Ramsay** repeated this experiment and examined the evolved gas spectroscopically. The spectrum of the gas was taken and it was analysed by **Crookes.** He confirmed that the spectrum besides other lines contained  $D_3$  line in the yellow region which was similar to  $D_3$  line observed in the sun's spectrum. Ramsay was, thus, first to find helium on the earth. Its vapour density was determined and it was found to be 2. It was also completely chemically inactive like argon.

#### Discovery of other inert gases

A new group, i.e., zero group was introduced in the periodic table to accommodate argon and helium. Argon was placed before potassium and helium was given position before lithium. Ramsay and Travers, thus, predicted that there must be an element before sodium also as to fill the position between helium and argon in the zero group. They further said that atmosphere might be the place where the new element could be searched.

Ramsay and Travers isolated about 16 litres of argon from atmosphere which now they began to suspect to be a mixture of a number of gases and they liquefied it. The liquid was then subjected to careful fractional evaporation under different reduced pressures. Each fraction was examined spectroscopically. From the first fraction, they isolated a new element which gave a number of red lines in the spectrum. It was named neon (meaning new). From the final fraction they isolated two new elements krypton (meaning hidden one) and xenon (meaning stranger) which gave new spectral lines in the spectrum.

The sixth member of the family, radon, was discovered in 1902 amongst the radioactive disintegration products of radium and other isotopes found in thorium and actinium radioactive series.

$$^{226}_{88}$$
Ra  $\xrightarrow{-\alpha}$   $^{222}_{86}$ Rn (Uranium series)  
 $^{224}_{88}$ Ra  $\xrightarrow{-\alpha}$   $^{220}_{86}$ Rn (Thorium series)  
 $^{223}_{88}$ Ra  $\xrightarrow{-\alpha}$   $^{219}_{86}$ Rn (Actinium series)

[The isotope  $^{220}_{86}$ Rn is also called thoron and the isotope  $^{219}_{86}$ Rn, actinon.] This discovery was announced by Dorn but Ramsay had also made similar observations simultaneously.

The last member of the family, ununoctium (118) has been recently discovered. Only three atoms of the new element with an average lifetime of 0.9 milliseconds have been produced so far. Scientists bombarded californium with calcium ions beam for many months.

## 13.4

# ISOLATION OF NOBLE GASES FROM THE ATMOSPHERE

Two methods are used for the separation of noble gases from the atmosphere. These are:

- (i) Chemico-physical method
- (ii) Physical method.

#### (i) Chemico-physical method

This involves the use of some chemical reagents for the removal of nitrogen and oxygen of the air and a physical method for the separation of individual noble gases from the gaseous mixture of five noble gases He, Ne, Ar, Kr and Xe. There are three chemical methods for the isolation of a mixture of all the noble gases from the atmospheric air. These methods are:

- (a) Ramsay and Rayleigh's first method.
- (b) Ramsay and Rayleigh's second method.
- (c) Modern method—Fisher and Ringe's method.

The first two methods are of historical importance only and are not used these days (already dealt in the discovery of argon).

#### Fisher and Ringe's method

This is the modern method for the large scale production of noble gases. Air free from moisture is circulated through an iron retort containing 90 parts of calcium carbide (CaC<sub>2</sub>) and 10 parts of anhydrous calcium chloride (CaCl<sub>2</sub>) kept at 800°C. Both oxygen and nitrogen are removed according to the following equations.

$$\begin{array}{c} \text{CaC}_2 + \text{N}_2 \longrightarrow & \text{CaCN}_2 + \text{C} \\ & \text{Calcium cyanamide} \end{array}$$
 
$$\begin{array}{c} 2\text{C} + \text{O}_2 \longrightarrow 2\text{CO} \\ 2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2 \\ \text{C} + \text{O}_2 \longrightarrow \text{CO}_2 \end{array}$$

Some of the CO<sub>2</sub> combines with calcium carbide.

$$2CaC_2 + 3CO_2 \longrightarrow 2CaCO_3 + 5C$$

The mixture of gases containing CO,  $CO_2$  and noble gases is passed over heated cupric oxide (CuO) when CO is oxidised to  $CO_2$ . The  $CO_2$  is absorbed by caustic potash solution when the gaseous mixture is passed through it.

$$CO + CuO \longrightarrow CO_2 + Cu$$
  
 $2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$ 

The gaseous mixture which now contains only noble gases is dried by bubbling through conc.  $H_2SO_4$  and is finally passed through tubes packed with phosphorus pentoxide and collected. The purpose of addition of  $CaCl_2$  is to reduce the reaction temperature from  $1000^{\circ}C$  to  $800^{\circ}C$ .

## 13.5 SEPARATION OF NOBLE GASES

#### Dewar's charcoal adsorption method

This method is based on the fact that activated coconut charcoal adsorbs different gases at different temperatures. The mixture of noble gases obtained from atmosphere is taken in a bulb filled with activated coconut charcoal and placed in a cold bath. The gases are allowed to remain in the bulb for about half an hour and unadsorbed gases are removed by a Toepler's pump and kept separately.

At -100°C, coconut charcoal adsorbs argon, krypton and xenon while helium and neon remain free. The unadsorbed helium and neon are brought in contact with another charcoal maintained at -180°C, when neon is adsorbed and helium is obtained in free state. Neon can be recovered from this charcoal on warming.

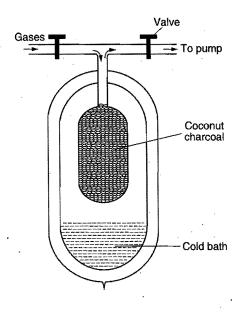
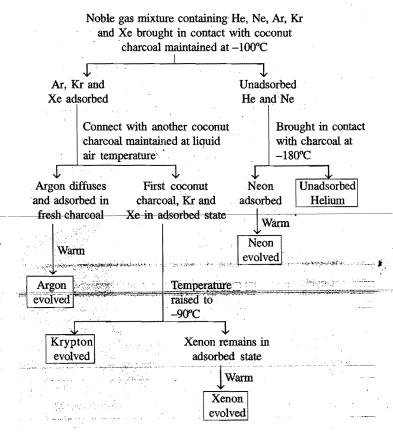


Fig. 13.1

When the charcoal containing Ar, Kr and Xe at -100°C is connected with another charcoal maintained at liquid air temperature, the argon diffuses into this charcoal from which it may be obtained by warming. After the separation of argon, the temperature of first charcoal is raised to -90°C when pure krypton is evolved. Xenon which remains behind is recovered by further warming the charcoal.

The whole process of separation can be summarised with the help of the flow sheet chart given ahead:



#### Physical method (Fractional distillation of liquid air):

Various constituents of liquid air possess different boiling points. These boiling points are:

Helium Neon Nitrogen Argon Oxygen Krypton Xenon -269°C -246°C -196°C -186°C -183°C -152°C -107°C

The sufficient difference in the boiling points of various constituents helps in carrying the fractional distillation of liquid air. This is done in **Claude's apparatus** (Fig. 13.2), which is especially used for the manufacture of liquid oxygen and liquid nitrogen but noble gases are also obtained as by-products.

Cold, compressed air enters the plant at the bottom. It ascends through the rectifier and through the tubes surrounded by liquid oxygen. It gets partially condensed into liquid which collects at the bottom.

The more volatile gases, mainly nitrogen get condensed in the receivers at the side.

The liquid collected at the bottom is pumped up and opens at the middle of the top rectifier. As it flows down, it meets the ascending gases from liquid oxygen. The contact between the two currents makes the descending liquid richer in oxygen which collects at the middle.

Liquid from the side tubes is pumped up to the top. Liquid is partially used for cooling purpose and partially for separation of helium and neon from nitrogen. At the various openings as shown in Fig. 13.2 (ahead), three fractions are obtained.

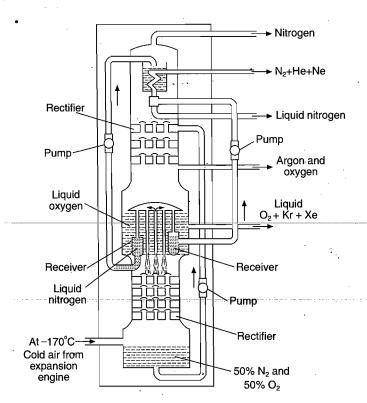


Fig. 13.2 Separation of the noble gases by fractionation

- 1. Helium and neon mixed with gaseous nitrogen.
- 2. Argon and oxygen in gaseous state above liquid oxygen.
- 3. Krypton and xenon present in liquid oxygen. The various noble gases are isolated from these fractions.
- (i) The gaseous mixture of He, Ne and nitrogen is passed through a spiral cooled by liquid nitrogen. Most of the nitrogen present in the gaseous mixture condenses. Nitrogen is completely removed by passing over CaC<sub>2</sub> at 1000°C. Helium and neon are separated by passing the mixture through a spiral cooled by liquid hydrogen (-253°C) when the neon is condensed leaving behind helium in free state.
- (ii) The second fraction containing argon and oxygen is fractionated by passing it around coils containing liquid nitrogen when oxygen is condensed and argon obtained in gaseous state.
- (iii) The liquid containing oxygen, krypton and xenon is fractionally distilled as there is wide difference in their boiling points.

## 13.6 USES OF NOBLE GASES

#### **Helium**

- (i) Since helium is light, non-inflammable, it is used in filling air-ships and balloons for weather study.
- (ii) Unlike nitrogen, helium is not soluble in blood even under high pressure, a mixture of 80% helium and 20% oxygen is used instead of ordinary air, by divers for respiration. The same mixture is used to assist breathing in asthama and other

respiratory diseases. If nitrogen is used along with oxygen in the cylinders of sea divers then nitrogen dissolves in blood at high pressure and create painful sensation called BENDS.

- (iii) Helium is used in research work for maintaining very low temperatures.
  - (iv) It is used in producing inert atmosphere.
  - (v) It is filled in tubes of aeroplane tyres.
  - (vi) It is used for food preservation.
- (vii) Nucleus of helium ( $\alpha$ -particles) are used as bombarding particles in artificial radioactivity.  $\alpha$ -particles are produced from helium using cyclotron.
  - (viii) It is used as filler in electric transformer.

#### Argon

- (i) It is widely used for filling incandescent metal filament electric bulbs.
- (ii) It is also used for filling radio-valves, rectifiers and fluorescent tubes. The neon-argon mixtures are used in advertising signs for various colours.
- (iii) It is used in producing inert atmosphere during welding and extraction of various metals.



Fig. 13.3 Noble gases in cathode ray discharge tubes characteristic glows. Argon glows blue.

#### Meon Neon

(i) It is used in neon discharge lamps and signs which are used for advertising purposes, since the neon lights (generally orange red) are visible from long distances and even visible



Fig. 13.4 Noble gases in cathode ray discharge tubes characteristic glows. Neon glows red.

through fog and mist. If mercury vapours are mixed with neon, a glow of blue or green colour is obtained. Neon lamps

are used over telephone tower, helipad and in music beat indicators of deck.

(ii) It is used in safety devices for protecting electrical instruments as it has a property of carrying exceedingly high currents under high voltages.

#### Krypton and xenon

These are used in filling incandescent metal filament electric bulbs. These gases are considered superior than argon for this purpose.

Krypton-85 is used to determine  $\sigma$  thickness of metal sheet and plastic sheets. Kr-85 is also used in regulating the voltage in electronic tubes.

#### Radon

- (i) It is used in radiotherapy of cancer.
- (ii) It is used to check the defects in steel castings.
- (iii) Photography of internal opaque materials is made with the help of radon.

### 13.7 COMPOUNDS OF NOBLE GASES

On account of stable electronic configuration, high ionisation potential and positive electron affinity, the noble gases are not expected to form chemical compounds with other elements. However, the recent researches have shown that under certain conditions these gases especially the higher ones are capable to form a few compounds. The only compounds known before 1962 were those observed in the discharge tubes or the hydrates and clathrates.

First theoretical support about compounds of inert gases was given by **Van Anthropove** in 1957 by taking into consideration of following compounds:

Molecule	Number of valence $e^-$ with central atom
PCl <sub>5</sub>	10e
SF <sub>6</sub>	12 <i>e</i>
$\mathbf{IF}_7$	14 <i>e</i> .

Central atom of above compounds have more than 8 electrons in valence shell (expanded octet). Thus, zero group elements can also form compounds by expanding their already existing octet.

- (i) Compounds formed in the discharge tubes: Boomer in 1925, reported the formation of WHe<sub>2</sub> by subjecting helium to electron bombardment using tungsten filament. In 1927, Manley reported that in presence of electric discharges mercury and helium combined to form combinations like HgHe<sub>2</sub> or HgHe<sub>10</sub>. Recent researches have shown that these reported compounds are not true chemical compounds.
- (ii) **Hydrates:** The hydrates of argon, krypton and xenon have been reported in literature. These are Ar-6H<sub>2</sub>O, Kr-6H<sub>2</sub>O, Xe-6H<sub>2</sub>O. The formation is due to dipole-dipole interaction. A

strong dipole water when brought in contact with a noble gas under high pressure and low temperature is likely to cause polarisation of the gas atom, *i.e.*, making it as a dipole which attracts the original dipole water.

Recent work of **Wiberg** and **Karbe** has rejected the idea of the formation of such hydrates.

(iii) Clathrates: Noble gases form a number of combinations in which gases are trapped into the cavities of crystal lattices of certain organic and inorganic compounds. These combinations are called **enclosure** or **cage** or **clathrate compounds**. (Latin: *clathrate* = enclosed or protected by cross-bars). The clathrates are normally non-stoichiometric compounds.

When quinol (o-dihydroxy benzene) is allowed to crystallise its solution in water in the presence of heavier noble gases such as argon, krypton or xenon under a pressure of 10-40 atmosphere, the noble gases get trapped within the lattice of quinol crystals. These crystals are quite stable. However, when heated or dissolved in solvent, the gas escapes.

The crystal structure with cavities is called the 'host' and the atom or molecule entrapped in it is called the 'guest'. The formation of a clathrate is only possible when the size of the cavity is such that it can fit in tightly the guest atom or molecule. Thus, helium and neon do not form clathrate compounds with quinol as the size of the cavity is more than the size of helium or neon atom.

(iv) Compounds discovered from 1962 onwards: Bartlett, in 1962, prepared a compound by reacting oxygen with a powerful oxidising agent platinum hexafluoride. The X-ray examination of the solid compound,  $O_2PtF_6$ , showed that it consisted of  $O_2^+$  and  $PtF_6^-$  ions. Bartlett thought that a similar compound could also be prepared with xenon since the ionisation potential of xenon is quite close to the ionisation potential of oxygen. When he reacted xenon with platinum hexafluoride, a red solid compound of composition,  $XePtF_6$  was obtained. Similarly,  $XeRuF_6$ ,  $XeRhF_4$  were also synthesized.

XePtF<sub>6</sub> was first real compound of any of the noble gases. The excitement caused by this discovery led to active search for other noble gas compounds and in a short time three fluorides of xenon, XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub> had been obtained as white crystalline solids.

**Xenon difluoride,** XeF<sub>2</sub>, is formed by heating a mixture of xenon and fluorine in molecular ratio 1 : 2 at 400°C in a nickel tube.

$$Xe + F_2 \xrightarrow{400^{\circ}C} XeF_2$$

Dioxygen fluoride reacts with Xe at about 118°C to give XeF<sub>2</sub>.

$$Xe + O_2F_2 \xrightarrow{118^{\circ}C} XeF_2 + O_2 \uparrow$$

In presence of mercury arc light, Xe and fluorine combine.

$$Xe + F_2 \xrightarrow{Mercury} XeF_2$$

It is a colourless, crystalline solid (m. pt. 140°C). It is decomposed by hydrogen and water.

$$XeF_2 + H_2 \longrightarrow Xe + H_2F_2$$
  
 $2XeF_2 + 2H_2O \longrightarrow 2Xe + 2H_2F_2 + O_2$ 

It acts as a strong oxidising agent.

$$XeF_2 + I_2 \xrightarrow{BF_3} 2IF + Xe$$
  
 $XeF_2 + 2HCl \longrightarrow Xe + H_2F_2 + Cl_2$ 

XeF<sub>2</sub> dissolves in HF but do not react with HF.XeF<sub>2</sub> forms addition compound with Lewis acids by itself acting as Lewis base, e.g.,

Lewis base + Lewis acid 
$$\longrightarrow$$
 Adduct
$$XeF_2 + 2SbF_5 \longrightarrow XeF_2 \cdot 2SbF_5$$
or
$$[XeF]^+ [Sb_2F_{11}]^-$$

$$XeF_2 + IF_5 \longrightarrow [XeF]^+ [IF_6]^-$$

 $XeF_2$  undergoes hydrolysis in aqueous alkaline solution, e.g.,

$$2XeF_2 + 4OH^- \longrightarrow 2Xe + 4F^- + 2H_2O + O_2$$

Lastly, XeF<sub>2</sub> acts as fluorinating agent also.

$$+ XeF_2 \longrightarrow \bigcirc^F + HF + Xe$$

$$2NO + XeF_2 \longrightarrow 2NOF + Xe$$

$$2NO_2 + XeF_2 \longrightarrow Xe + 2NO_2F$$

Note: Vessels of monel metal (alloy of nickel) are used to store XeF<sub>2</sub>.

**Xenon tetrafluoride,** XeF<sub>4</sub>, is formed by heating a mixture of xenon and fluorine in the molecular ratio 1: 10 at 400°C in a nickel tube.

$$Xe + 2F_2 \xrightarrow{400^{\circ}C} XeF_4$$

It is never synthesized in pure form because its formation is accompanied with the formation of XeF<sub>2</sub> and XeF<sub>6</sub>.

It is a colourless, crystalline solid (m. pt. 107°C). It undergoes sublimation. It is reduced by hydrogen, mercury and boron trichloride.

$$XeF_4 + 2H_2 \longrightarrow Xe + 2H_2F_2$$
  
 $XeF_4 + 2Hg \longrightarrow Xe + 2HgF_2$   
 $3XeF_4 + 4BCl_3 \longrightarrow 4BF_3 + 3Xe + 6Cl_2$ 

It forms a highly explosive solid, xenon trioxide (XeO<sub>3</sub>) when treated with water.

$$2XeF_4 + 3H_2O \longrightarrow Xe + XeO_3 + 3H_2F_2 + F_2$$

It is soluble in fluoroacetic acid ( $CF_3COOH$ ). When it is heated with excess of Xe it changes to  $XeF_2$ .

$$XeF_4 + Xe(excess) \xrightarrow{Warm} 2XeF_2$$

It undergoes addition reactions like XeF<sub>2</sub>, forming adducts.

Other Lewis acids like PF<sub>5</sub>, AsF<sub>5</sub>, SbF<sub>5</sub>, NbF<sub>5</sub>, RuF<sub>5</sub>, OsF<sub>5</sub> also undergo similar addition reactions.

Like  $XeF_2$ , xenon tetrafluoride also acts as fluorinating agent, e.g.,

$$XeF_4 + Pt \longrightarrow Xe + PtF_4$$
  
 $4NO + XeF_4 \longrightarrow Xe + 4NOF$   
 $4NO_2 + XeF_4 \longrightarrow Xe + 4NO_2F$ 

**Xenon hexafluoride,** XeF<sub>6</sub>, is formed by heating xenon and fluorine in molecular ratio 1: 20 under pressure in a nickel tube.

$$Xe + 3F_2 \xrightarrow{300^{\circ}C} XeF_6$$

It is a colourless crystalline solid (m. pt. 49.5°C). It is reduced by H<sub>2</sub>, HCl and NH<sub>3</sub>.

$$XeF_6 + 3H_2 \longrightarrow Xe + 3H_2F_2$$
  
 $XeF_6 + 6HCl \longrightarrow Xe + 3H_2F_2 + 3Cl_2$   
 $XeF_6 + 8NH_3 \longrightarrow Xe + 6NH_4F + N_2$ 

The hydrolysis of XeF<sub>6</sub> with water yields new compounds.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + H_2F_2$$
  
 $XeOF_4 + H_2O \longrightarrow XeO_2F_2 + H_2F_2$   
 $XeO_2F_2 + H_2O \longrightarrow XeO_3 + H_2F_2$ 

Like other xenon fluorides, XeF<sub>6</sub> is also stored in nickel alloy (monel metal) vessel. It cannot be stored in glass vessel because silica in glass reacts with XeF<sub>6</sub>.

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$
  
 $2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$   
 $2XeOF_4 + 2SiO_2 \longrightarrow 2XeO_3 + 2SiF_4$ 

XeF<sub>6</sub> dissolves in HF according to the following reaction

$$XeF_6 + HF \longrightarrow [XeF_5]^+ [HF_2]^-$$

XeF<sub>6</sub> undergoes thermal decomposition

$$2XeF_6 \longrightarrow XeF_2 + XeF_4 + 3F_2$$

Like XeF<sub>2</sub> and XeF<sub>4</sub>, XeF<sub>6</sub> also acts as fluorinating agent. XeF<sub>6</sub> has strongest fluorinating tendency. XeF<sub>6</sub> undergoes addition reactions with Lewis acids, *e.g.*,

$$XeF_6 + AsF_5 \longrightarrow [XeF_5]^+ [AsF_6]^-$$
  
 $XeF_6 + BF_3 \longrightarrow [XeF_5]^+ [BF_4]^-$   
 $XeF_6 + NaF \longrightarrow NaXeF_7$   
 $2NOF + XeF_6 \longrightarrow [NO]_2^{2+} [XeF_8]^{2-}$ 

Hexafluoride undergoes hydrolysis in strongly alkaline medium.

$$2XeF_6 + 16OH^- \longrightarrow 8H_2O + 12F^- + XeO_6^{4-} + Xe + O_2$$

#### Structure of Xenon Fluorides

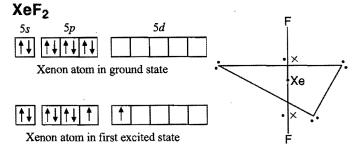
The bonding in these compounds is covalent. The formation involves the unpairing of *p*-orbitals and promotion of electron or electrons to the vacant *d*-orbitals in the outermost shell. In

the excited state, the xenon atom undergoes hybridization forming definite configurations. The unpaired electrons in the hybrid orbitals form covalent (sigma) bonds with fluorine atoms.

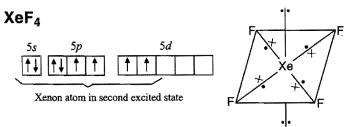
The hybridization of xenon atom and shapes of different fluorides can be predicted with the help of following generalisation:

Hybridization = 1/2 [No. of electrons in the valence shell of central atom + No. of monovalent atoms surrounding the central atom—charge on the cation + charge on the anion]

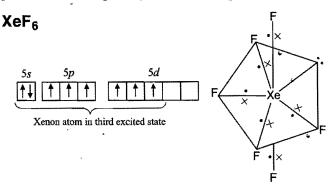
Molecule	Total numb	er of orbitals	Hybridi-	Shape
·	undergoing	hybridization	zation	
XeF <sub>2</sub>	1/2[8 + 2	-0+0]=5		Linear .
XeF <sub>4</sub>	1/2[8+4]	-0+0]=6	$sp^3d^2$	Square planar
XeF <sub>6</sub>		-0+0]=7	$sp^3d^3$	Distorted octahedral



In the formation of  $XeF_2$ ,  $sp^3d$  hybridization occurs which gives the molecule a trigonal bipyramidal structure. The xenon and two fluorine atoms lie in a straight line while the three equatorial positions are occupied by the three lone pairs of electrons.



In the formation of  $XeF_4$ ,  $sp^3d^2$  hybridization occurs which gives the molecule an octahedral structure. The xenon and four fluorine atoms are co-planar while the two equatorial positions are occupied by the two lone pairs of electrons.



In the formation of  $XeF_6$ ,  $sp^3d^3$  hybridization occurs which gives the molecule a pentagonal bipyramidal structure. Six positions are occupied by fluorine atoms and one position is occupied by a lone pair of electrons.

Due to presence of lone pair, distortion in structure takes place. The actual structure is distorted octahedral.

#### HYBRIDIZATION AND SHAPES OF XENON FLUORIDES

Molecule	pairs of	No. of lone pairs of electrons	Total electron pairs	Hybridi- zation	Structure	Actual shape
XeF <sub>2</sub>	2	3	5	sp <sup>3</sup> d	Trigonal bipyramidal	Linear
XeF <sub>4</sub>	4	2	6	$sp^3d^2$	Octahedral	Square planar
XeF <sub>6</sub>	6	1	. 7	$sp^3d^3$	Pentagonal bipyramidal	Distorted

Krypton also forms krypton difluoride (KrF<sub>2</sub>) and krypton tetrafluoride (KrF<sub>4</sub>) under suitable conditions, RnF<sub>2</sub> has also been prepared. However, all attempts have failed to prepare similar compounds in the case of He, Ne and Ar.

Xenon oxides and xenon oxyfluorides: Xenon forms two oxides, xenon trioxide (XeO<sub>3</sub>) and xenon tetroxide (XeO<sub>4</sub>).

Xenon trioxide is obtained by hydrolysis of  $XeF_4$  and  $XeF_6$  with water.

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 12H_2F_2 + 3O_2$$
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 3H_2F_2$$

Xenon tetroxide is obtained by the action of anhydrous sulphuric acid on barium perxenate.

$$Ba_2 [XeO_6] + 2H_2SO_4 \longrightarrow 2BaSO_4 + XeO_4 + 2H_2O$$

XeO<sub>3</sub> is a colourless explosive solid. It is a powerful oxidising agent. It oxidises Pu<sup>2+</sup> to Pu<sup>4+</sup> in the presence of H<sup>+</sup> ions.

$$3Pu^{2+} + XeO_3 + 6H^+ \longrightarrow 3Pu^{4+} + Xe + 3H_2O$$

 $XeO_3$  reacts with aqueous alkali to form the hydrogen xenate ion (HXeO $_4$ ) which slowly disproportionates to give xenon and perxenate ion (XeO $_6$ ) in which xenon is present in +8 oxidation state.

$$XeO_3 + OH^- \longrightarrow HXeO_4^-$$
  
 $2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-} + Xe + 2H_2O + O_2$ 

Perxenate solutions are yellow and powerful oxidising agents.  $XeO_4$  is less stable than  $XeO_3$  and decomposes into xenon and oxygen.

$$XeO_4 \longrightarrow Xe + 2O_2$$

Xenon oxyfluorides: A number of oxyfluorides are known.

- (i) Xenon oxydifluoride (XeOF<sub>2</sub>)
- (ii) Xenon dioxydifluoride (XeO<sub>2</sub>F<sub>2</sub>)
- (iii) Xenon oxytetrafluoride (XeOF<sub>4</sub>)
- (iv) Xenon dioxytetrafluoride (XeO<sub>2</sub>F<sub>4</sub>)
- (v) Xenon trioxydifluoride (XeO<sub>3</sub>F<sub>2</sub>).

Some of the oxyfluorides are obtained by partial hydrolysis of  $XeF_4$  and  $XeF_6$ .

$$XeF_4 + H_2O \longrightarrow XeOF_2 + H_2F_2$$
  
 $XeF_6 + H_2O \longrightarrow XeOF_4 + H_2F_2$   
 $XeOF_4 + H_2O \longrightarrow XeO_2F_2 + H_2F_2$ 

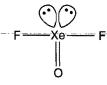
Shapes of xenon oxides and xenon oxyfluorides: The shapes of oxygen containing compounds of xenon are correctly predicted on the basis of Valence Bond Theory and Valence Shell Electron Pair Repulsion Theory.

In this case  $\pi$ -electrons must be subtracted in counting the total number of electron pairs in the valence shell of central atom.

(i) 
$$XeOF_2$$
:  $\pi$  bond = 1

Total\_number\_of\_electron\_pairs = 6... Number of lone pairs = 2

Shape  $\rightarrow$  T-shape geometry  $(sp^3d)$ 



Structure

## Total No. of orbitals undergoing hybridization

Hybridization

XeOF<sub>2</sub>

$$1/2[8+2-0+0] = 5$$

 $sp^3d$ 

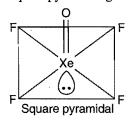
(ii) XeOF<sub>4</sub>:

 $\pi$  bond = 1

Total number of electron pairs = 7

Number of lone pair = 1

Shape  $\rightarrow$  Square pyramidal geometry  $(sp^3d^2)$ 



Structure

## Total No. of orbitals undergoing hybridization

Hybridization

XeOF<sub>4</sub>

$$1/2[8+4-0+0] = 6$$

 $sp^3d^2$ 

(iii) XeO<sub>3</sub>:

$$\pi$$
 bonds = 3

Total number of electron pairs = 7

Number of lone pair = 1

Shape  $\rightarrow$  Pyramidal geometry  $(sp^3)$ 



Pyramidal

Structure

Total No. of orbitals undergoing hybridization

Hybridization

 $XeO_3$ 

$$1/2[8+0-0+0]=4$$

 $sp^3$ 

(iv) XeO<sub>4</sub>:

 $\pi$  bonds = 4

Total number of electron pairs = 8

Shape  $\rightarrow$  Tetrahedral  $(sp^3)$ 

Structure

Total No. of orbitals undergoing hybridization

Hybridization

XeO<sub>4</sub>

$$1/2[8+0-0+0]=4$$

 $sp^3$ 

(v)  $XeO_2F_2$ :  $\pi$  bonds = 2

Total number of electron pairs = 7

Number of lone pair = 1

Shape  $\rightarrow$  Trigonal bipyramid  $(sp^3d)$ 



Structure

Total No. of orbitals undergoing hybridization

Hybridization

XeO<sub>2</sub>F<sub>2</sub>

$$1/2[8 + 2 - 0 + 0] = 5$$

 $sp^3d$ 

# 13.8 IMPORTANCE OF NOBLE GASES IN THEORETICAL CHEMISTRY

Noble gases have played an important role in the development of various subjects of theoretical chemistry.

- (i) Improvement in periodic table: Insertion of zero group between highly electronegative halogens and highly electropositive alkali metals improved the periodic table. Zero group occupies the intermediate position between two extreme groups of elements.
- (ii) In establishing the scheme for the arrangement of electrons in atoms: All noble gases except helium have 8 electrons in the outermost energy shell. This configuration accounts for the inertness of these elements. It led Bohr and Bury to assume that the outermost energy shell of any stable atom cannot have more than 8 electrons.
- (iii) In the development of electronic theory of valency: All elements tend to acquire stable configuration during chemical union. This is possible when they acquire noble gas configuration, *i.e.*, 8 electrons in the outermost energy shell. This occurs either by transference of electrons from one atom to another (electrovalency) or by sharing of electrons (covalency) or by contributing both electrons to be shared by only one atom (coordinate valency).
- (iv) Group displacement law in radioactivity: α-particles are emitted by the disintegration of radioactive elements. Alphaparticles are actually helium nuclei. It has proved useful in formulating the theory of radioactive disintegration and the group displacement law.
- (v) In the discovery of isotopes: Neon was the first non-radioactive element whose isotopes were first of all separated. On this basis, it was concluded that other elements

may also consist of a mixture of two or more isotopes. This has helped in the discovery of many new isotopes.

#### 13.9 DETERMINATION OF ATOMIC MASS OF A NOBLE GAS

Chemical equivalent masses of noble gases cannot be determined by usual methods as these are chemically inert. Thus, the following relationship cannot be used for the determination of atomic masses of noble gases.

Atomic mass = Equivalent mass  $\times$  valency

The molecular mass of any gaseous element is related with its atomic mass by the following relationship:

Molecular mass = Atomicity  $\times$  Atomic mass

The atomicity of noble gases is unity.

Thus, Molecular mass = Atomic mass

Molecular mass can easily be calculated if vapour density is determined experimentally.

Mol. mass =  $2 \times$  vapour density

At. mass =  $2 \times$  vapour density or



# SUMMARY AND IMPORTANT POINTS TO REMEMBER



- 1. The zero or 18th group consists of seven elements—helium, neon, argon, krypton, xenon, radon and ununoctium. This group was unknown when Mendeleev presented the periodic table and has been inserted only at a later stage. It occupies an intermediate position between electronegative elements of VIIA (17th) and electropositive elements of IA (1st) groups.
- 2. The members of zero group are the end members of respective periods of periodic table. This is the only group of the periodic table, all members of which are gases and chemically inactive under ordinary conditions. These are collectively called as inactive or inert gases. However, these are now called noble gases as some compounds of these gases have been obtained under specific conditions. They are also termed zerovalent elements because they show zero valency.
- 3. Except radon which is radioactive, all other members are present in atmosphere in minute quantities. Thus, they are termed rare gases of atmosphere. They form about 1% by volume of the air. Argon is the priamoal constituent.
- All the noble gases have stable configuration. Except helium which has  $1s^2$  configuration, rest has 8 electrons, i.e.,  $s^2p^6$ configuration in the outer shell. They have no tendency either to lose, gain or share electrons with the atoms of other
- 5. Ionisation potential values are high. However, decreases on moving down the group.
- Electron affinity values are positive.
- 7. They all are colourless, odourless and tasteless gases. All are mono-atomic in nature as  $C_p/C_v$  value for every gas is 1.66. All have low values of melting and boiling points. The values increase as the atomic number increases.

Among the known elements, helium has got the lowest melting and boiling points.

- 8. These gases have fairly high electrical conductivity. They produce characteristic coloured lights when an electrical discharge is passed through at low temperature.
- 9. These gases are relatively difficult to be liquefied. Liquefaction becomes easier from He to Xe.
- 10. These gases are sparingly soluble in water. The solubility increases with increasing atomic number.
- 11. Except He, these gases can be adsorbed by coconut charcoal at suitable temperatures.

- 12. Noble gases always occur in the free state. The chief sources are:
  - (a) Air
  - (b) Natural gas: contains up to 7% helium.
  - (c) Radioactive minerals : only He.

  - (d) Spring water—dissolved He, Ne and Ar. (e) Radon—radioactive decay  $^{226}_{88}$ Ra  $\longrightarrow$   $^{222}_{86}$ Rn +  $^{4}_{2}$ He.
- 13. Argon—Greek word-argos meaning lazy or inert.

Helium—Greek word-helios meaning sun. First reported on the surface of sun.

Neon-Meaning new.

Krypton—Meaning hidden one.

Xenon-Meaning stranger.

The credit for the discovery of above gases goes to Ramsay and Travers. Radon was discovered by Dorn.

- 14. Two methods are used for the separation of noble gases from the atmosphere.
  - (i) Chemico-physical method: It involves the use of some chemical reagents for the removal of nitrogen and oxygen of the air and a physical method for the separation of individual noble gases from the gaseous mixture. The modern method for isolation of gaseous mixture of noble gases from air is:

Fisher-Ringe's method: Air free from moisture and CO<sub>2</sub> is passed over a mixture in an iron retort containing 90% CaC<sub>2</sub> and 10% CaCl<sub>2</sub> anhydrous kept at 800°C. Both O2 and N2 are removed.

$$\begin{array}{ccc}
CaC_2 + N_2 \longrightarrow CaCN_2 + C \\
2C + O_2 \longrightarrow 2CO \\
2CO + O_2 \longrightarrow 2CO_2
\end{array}$$
or  $C + O_2 \longrightarrow CO_2$ 

The mixture of gases containing CO, CO<sub>2</sub> and noble gases is passed over heated CuO when CO is oxidised to CO<sub>2</sub>. The CO<sub>2</sub> is absorbed in caustic potash solution and the unabsorbed gases are dried over P2O5.

Noble gases mixture is separated into individual gases by Dewar's charcoal adsorption method. At -100°C, coconut charcoal adsorbs argon, krypton and xenon. The unadsorbed He and Ne are separated at −180°C, when neon is adsorbed and helium is left free. Neon is recovered by warming the charcoal. When the charcoal containing Ar, Kr and Xe is connected with another charcoal at liquid air temperature, the argon diffuses to new charcoal from which it can be obtained by warming. When the temperature of first charcoal is raised to -90°C, krypton is set free and on further warming, xenon is recovered.

- (ii) Physical method of separation, i.e., distillation of liquid air. For fractional distillation of liquid air claude's apparatus is used. Three fractions are obtained:
  - (a) Helium and neon mixed with gaseous nitrogen.
  - (b) Argon and oxygen in gaseous state.
  - (c) Krypton and xenon present in liquid oxygen.

    These mixtures are further fractionally separated into individual members.
- **15.** (a) Since helium is light and non-inflammable, it is filled in filling airships and balloons.
  - (b) A mixture of 80% helium and 20% oxygen is used instead of ordinary air for respiration by sea divers and asthama patients.
  - (c) Helium is used for inflating the tyres of big aeroplanes in place of air being lighter.
  - (d) Argon is used in creating inert atmosphere during extraction of various metals and welding.
  - (e) Argon is used for filling incandescent metal filament electric bulbs, radio-valves and fluorescent tubes.
  - (f) Liquid helium is used as cryogenic.
  - (g) Neon signs for advertising contain neon gas.
  - (h) Radon is used in radiotherapy of cancer.
- **16.** Until 1962, no real compound of noble gases was known. In 1962, it was observed that oxygen reacts with PtF<sub>6</sub> to form a compound O<sub>2</sub><sup>+</sup>[PtF<sub>6</sub>]<sup>-</sup>.

Since  $O_2$  molecule has ionisation energy  $[O_2 \longrightarrow O_2^+ + e;$  1166 kJmol<sup>-1</sup>] almost same as that of Xe [Xe  $\longrightarrow$  Xe<sup>+</sup> + e; 1170 kJmol<sup>-1</sup>], Neil Bartlett suggested that PtF<sub>6</sub> should show a similar reaction with xenon. He then tried to react these two at 298 K. He actually obtained the compound, XePtF<sub>6</sub>.

XePtF<sub>6</sub> was first real compound of any of the noble gases and in a short time three fluorides of xenon, XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub> has been obtained as crystalline solids.

$$Xe + F_2 \xrightarrow{\begin{array}{c} 1:2 \text{ 400°C} \\ \text{Ni} \end{array}} XeF_2$$

$$\xrightarrow{\begin{array}{c} 1:10 \text{ 400°C} \\ \text{Ni} \end{array}} XeF_4$$

$$\xrightarrow{\begin{array}{c} 1:20 \text{ 300°C} \\ \text{50 atm.} \end{array}} XeF_6$$

Xenon fluorides react with hydrogen, water and fluoride ion acceptors like, PF<sub>5</sub>, SbF<sub>5</sub> and AsF<sub>5</sub>, etc.

$$XeF_2 + H_2 \longrightarrow Xe + H_2F_2;$$
  
 $2XeF_2 + 2H_2O \longrightarrow 2Xe + 2H_2F_2 + O_2;$   
 $XeF_4 + 2H_2 \longrightarrow Xe + 2H_2F_2;$   
 $2XeF_4 + 3H_2O \longrightarrow Xe + XeO_3 + 3H_2F_2 + F_2;$ 

$$\begin{split} XeF_6 + 3H_2 &\longrightarrow Xe + 3H_2F_2; \\ XeF_6 + H_2O &\longrightarrow XeOF_4 + H_2F_2; \\ XeF_2 + IF_5 &\longrightarrow [XeF]^+ [IF_6]^-; \\ XeOF_4 + H_2O &\longrightarrow XeO_2F_2 + H_2F_2; \\ XeF_4 + SbF_5 &\longrightarrow [XeF_3]^+ [SbF_6]^-; \\ XeO_2F_2 + H_2O &\longrightarrow XeO_3 + H_2F_2; \\ XeF_6 + AsF_5 &\longrightarrow [XeF_5]^+ [AsF_6]^- \end{split}$$

- 17. Xenon forms two oxides xenon trioxide (XeO<sub>3</sub>) and xenon tetroxide (XeO<sub>4</sub>). Xenon trioxide is a colourless explosive solid. It is a powerful oxidising agent. Xenon tetroxide is less stable than XeO<sub>3</sub> and decomposes into Xe and O<sub>2</sub>.
- 18. A number of oxyfluorides of xenon are known:
  - (i) Xenon oxydifluoride, XeOF<sub>2</sub>
  - (ii) Xenon dioxydifluoride, XeO<sub>2</sub>F<sub>2</sub>
  - (iii) Xenon oxytetrafluoride, XeOF<sub>4</sub>
  - (iv) Xenon dioxytetrafluoride, XeO<sub>2</sub>F<sub>4</sub>
  - (v) Xenon trioxydifluoride, XeO<sub>3</sub>F<sub>2</sub>

19.	Molecule	Hybridization of central atom	No. of lone pair(s) around central atom	Shape
	XeF <sub>2</sub>	$sp^3d$	3	Linear,
		-	i e	Two o bonds
	XeF <sub>4</sub>	$sp^3d^2$	2.	Square planar,
				Four σ bonds
	XeF <sub>6</sub>	$sp^3d^3$	1	Distorted octahedral,
				· Six σ bonds
	$XeO_3$	$sp^3$	1	Pyramidal, Three σ
				and three π bonds
	$XeO_4$	$sp^3$		Tetrahedral, Four σ
_				and four $\pi$ bonds
	$XeOF_2$	$sp^3d$	2	T-shaped, Three σ
				and one $\pi$ bond
	XeOF <sub>4</sub>	$sp^3d^2$	1	Square pyramidal, Five
		•		$\sigma$ and one $\pi$ bond
	$XeO_2F_2$	$sp^3d$	1	See-Saw, Four σ
				and two π bonds

- **20.** No compound of He and Ne is known so far. Helium and neon do not form any clathrate due to small size. Ar, Kr and Xe form clathrates.
- 21. Noble gases have played an important role in the development of various subjects of theoretical chemistry such as:
  - (a) Improvement in periodic table by introducing zero group.
  - (b) In establishing the scheme for the arrangement of electrons in various energy shells of atoms.
  - (c) In the development of electronic theory of valency.
  - (d) Group displacement law in radioactivity.
  - (e) In the discovery of isotopes.



# PRACTICE PROBLEMS



#### Subjective Type Questions

- 1. Name the noble gas which:
  - (i) is abundant in atmosphere
  - (ii) is found in natural gas
  - (iii) is radioactive
  - (iv) is not adsorbed in coconut charcoal
  - (v) highest boiling point.
- (a) Which was the first noble gas compound synthesized? Who prepared it?
  - (b) Which one of the following does not exist?
    - (i)  $XeOF_4$  (ii)  $NeF_2$  (iii)  $XeF_2$  (iv)  $XeF_6$
  - (c) Name the chemical compound which can remove both nitrogen and oxygen from pure and dry air.
- 3. (a) What were the reasons for late discovery of noble gases?
  - (b) What made Rayleigh suspect that there may be an additional element in air?
  - (c) Why noble gas compounds are formed only with O<sub>2</sub> and
- Complete the following reactions:
  - (i)  $XeF_4 + H_2O \longrightarrow$
  - (ii)  $XeF_2 + H_2 \longrightarrow$
  - (iii)  $XeF_6 + SiO_2 \longrightarrow$
  - (iv)  $XeF_6 + NH_3 \longrightarrow$
  - (v)  $XeF_6 + H_2O \longrightarrow$
  - (vi)  $XeF_6 + SbF_5 \longrightarrow$
- Answer the following with relevant reason.
  - (i) Why the group in which inert gases are accommodated was called zero group?

[Hint: Inert gases do not show chemical activity under ordinary conditions due to possession of completed outermost shell, i.e., they show zero valency. On account of zero valency, the group in which inert gases were placed was called zero group.]

(ii) Why the zero group elements do not form compounds under ordinary conditions?

[Hint: Zero group elements have complete electronic configuration of their outermost shells, i.e.,  $s^2p^6$  (except helium which has 1s<sup>2</sup>), hence they do not have any tendency either to lose or accept electron/electrons or share electrons with other atoms.]

(iii) Xenon has closed shell configuration but is known to give compounds with fluorine.

[Hint: Xenon atom has large size and lower ionisation potential in comparison to He, Ne, Ar and Kr. The outermost energy shell has d-orbitals. The paired electrons of valency shell can be unpaired and the electrons are shifted to d-orbitals under suitable conditions. The unpaired electrons are shared by fluorine atoms and covalent bonds are formed. In this way, xenon forms compounds with fluorine.]

- (iv) Helium and neon do not form compounds with fluorine.
  - [Hint: He and Ne are smaller atoms and possess very high ionisation potential. Both do not have d-orbitals in their valency shells. Thus, the paired orbitals of valency shell cannot be unpaired. In absence of singly occupied orbitals, no sharing is possible with other atoms. Hence, no compounds are formed by He and
- (v) The boiling points of noble gases increase with increase in atomic number.

Hint: van der Waals' forces of attraction among molecules increase with the increase of atomic masses. Thus, higher energy is required to separate these molecules as to get gaseous state. Hence, the boiling points increase with increase of atomic masses.]

- (vi) Why neon is used in warning signal illuminations? [Hint: Neon lights are visible from long distances. The lights are even visible during fog and mist conditions.]
- (vii) A mixture of He and O2 is used for respiration by sea divers.

[Hint: Unlike nitrogen, helium is not soluble in blood even under high pressure.]

(viii) Why helium and neon do not form clathrate compounds with quinol?

[Hint: The size of the cavities formed during crystallisation of quinol is more than the size of helium and neon atoms.]

(ix) Why xenon does not form fluorides such as XeF, XeF<sub>3</sub> or XeF<sub>5</sub>?

[Hint: By unpairing of one paired orbital, two singly occupied orbitals come into existence. Thus, either two or four or six singly occupied orbitals can be formed instead of one or three or five singly occupied orbitals. Hence, XeF or XeF<sub>3</sub> or XeF<sub>5</sub> are not formed.]

Draw the molecular structures of XeF<sub>2</sub>, XeF<sub>4</sub> and XeO<sub>2</sub>F<sub>2</sub> indicating the location of lone pair(s) of electrons.

[I,I,T, 2000]

What is the hybridization of xenon in, geometry and shape of the following molecules?

XeOF<sub>2</sub>, XeOF<sub>4</sub>, XeO<sub>2</sub>F<sub>2</sub> and XeF<sub>6</sub>.

|Hint:

:	Molecule	Hybridization of xenon	Geometry	Shape
	XeOF <sub>2</sub>	$sp^3d$	Trigonal bipyramidal	T-shaped
	XeOF <sub>4</sub>	$sp^3d^2$	Octahedral	Square pyramidal
	XeO <sub>2</sub> F <sub>2</sub>	sp <sup>3</sup> d	Trigonal bipyramidal	Distorted trigonal bipyramidal
	XeF <sub>6</sub>	$sp^3d^3$	Pentagonal bipyramidal	Distorted octahedral

**8.** Does the hydrolysis of XeF<sub>6</sub> lead to a redox reaction?

[Hint: When XeF<sub>6</sub> undergoes hydrolysis, it forms XeOF<sub>4</sub>, XeO<sub>2</sub>F<sub>2</sub> and XeO3 as products. In these compounds, there is no change in oxidation state of Xe. Thus, the hydrolysis of XeF<sub>6</sub> is not a redox reaction.]

#### Matching Type Questions

#### Match the following:

- (i) Helium
- (a) Lazy
- (ii) Neon
- (b) Hidden one
- (iii) Argon
- (c) Stranger
- (iv) Krypton
- (d)  $1s^2$ ,  $2s^22p^6$
- (v) Xenon
- (e) Sun's element
- (vi) Radon
- (f) Radioactive

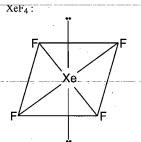
#### Answers: Subjective Type Questions

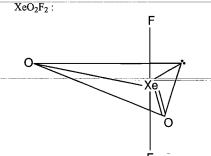
- (i) Argon
- (ii) Helium (iii) Radon or ununoctium
  - (iv) Helium (v) Xenon
- (a) XePtF<sub>6</sub>, Bartlett (b) NeF<sub>2</sub>
- (c) CaC<sub>2</sub> (Calcium Carbide)
- (a) Chemical inertness and rare abundance
  - (b) Density of nitrogen isolated from air was always higher than the nitrogen obtained chemically.
  - (c) Because noble gases have extremely low reactivity, they need strongest oxidising agents to form compounds.
- (i)  $2XeF_4 + 3H_2O \longrightarrow Xe + XeO_3 + 6HF + F_2$  (It undergoes disproportionation.)
  - $XeF_2 + H_2 \longrightarrow Xe + 2HF$
  - $2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$ 

    - $2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$   $2XeO_2F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$ Explosive
  - $XeF_6 + 8NH_3 \longrightarrow Xe + 6NH_4F + N_2$
  - $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$ (v)
  - $XeF_6 + SbF_3 \longrightarrow [XeF_5]^+ [SbF_6]^-$

[Addition ionic product is formed.]

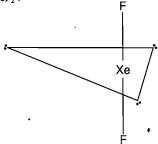
6.





Trigonal bipyramid

 $XeF_2$ :



Answers: Matching Type Questions

(i-e); (ii-d); (iii-a); (iv-b); (v-c); (vi-f).

# **OBJECTIVE QUESTIONS**

				:
		$\sim$		

**Set I:** This set contains questions with single correct answer.

1.		ery of noble gases is given to	_	16.	The formation of XeF <sub>4</sub> is	due	to hybridiza	tion of
	(a) Cavendish		Ц		excited xenon.	m	a > 3	
	(b) Ramsay				(a) $sp^2$	Ц	(b) $sp^3$	빌
	(c) Rayleigh				(c) $sp^3d$		(d) $sp^3d^2$	
•	(d) Frankland and Lockye			17.	Xenon difluoride is:	_		punny
2.	Noble gases are chemically	-			(a) linear		(b) angular	_ ∐ .
		☐ (b) low boiling points			(c) trigonal		(d) pyramidal	Q,
	(c) closed valency shell			18.	The mixture which is use			
3.		most abundant in air?					(b) helium and O <sub>2</sub>	
	• /	□ (b) He			(c) argon and O <sub>2</sub>			
		$\square$ (d) $CO_2$		19.	The gas which is filled in		~ <u>.</u>	
4.	The lightest gas which is			-	(a) $H_2$		(b) He	
		$\square$ (b) $N_2$			(c) Ar		(d) O <sub>2</sub>	
	(c) Ar	☐ (d) He		20.	A radioactive element w	hich	can decay to give two	noble
5.	If one litre of air is passed	l repeatedly on hot copper and	d hot		gases, is:		222	
	magnesium till no further o	decrease in volume takes place	e, the		(a) $U^{238}$		(b) $Th^{232}$	
	volume of residual gas we	ould be about:			(c) $Ac^{239}$		(d) Ra <sup>226</sup>	
	(a) 200 mL	□ (b) 100 mL		21.	A noble gas which is no			coal is:
	(c) 10mL	☐ (d) zero			(a) He		(b) Ne	
6.	Radon is a:				(c) Ar		(d) Ra	
	(a) drug	☐ (b) explosive		22.	The coloured discharge	tut	e for advertisement	mainly
	(c) trade name of nylon	☐ (d) noble gas		]	contains:			•
7.		nd which can remove both ox	ygen	1	(a) xenon		(b) helium	
		hen it is passed over it at 100			(c) neon		(d) argon	
	•	☐ (b) CaCl <sub>2</sub>		23.	Maximum number of cor	mpou	· · · · · · · · · · · · · · · · · · ·	ase of:
		$\square$ (d) Ca(CN) <sub>2</sub>			(a) neon			
8.	The $C_p/C_v$ ratio for noble			-	(c) krypton		(d) argon	
-		□ (b) 1.66		24	XeF <sub>6</sub> on complete hydro			_
		☐ (d) 1.0			(a) Xe		(b) XeO <sub>2</sub>	
9.	The inert gas obtained from				(c) XeO <sub>3</sub>		(d) $XeO_4$	
	(a) He	☐ (b) Ne		25	XeF <sub>4</sub> exists as und			
	(c) Ar	□ (d) Kr		20.	(a) solid		(b) liquid	
10.	• •	loes not react with fluorine?			(c) gas		_	
	_	□ (b) Xe		26	In solid argon, the atom		' '	
	3 -	☐ (d) all of these		20.	(a) ionic bonds		(b) hydrogen bonds	
11.	The gas with lowest boili				(c) van der Waals' force			
		(b) helium		27	The oxidation state of			
		☐ (d) argon		21.	Na <sub>4</sub> XeO <sub>6</sub> are respectivel		n atom in Acr4, tiAc	O4 and
12.	The element having high						41.	,
	(a) hydrogen	☐ (b) oxygen			(a) $+4, +6, +6$		(b) $+4, +6, +7$	
	(c) nitrogen	☐ (d) helium			(c) $+4, +6, +8$		(d) $+4$ , $+5$ , $+8$	
13.	Claude's apparatus is used	d for the isolation of	from	28.	Which of the following is	s used	d to attain very low temp	perature
	liquid air.		,		during cryoscopic studie	es ?		
	(a) liquid oxygen only	$\Box$ (b) liquid nitrogen only			(a) Ar		(b) He	
	(c) noble gases only	☐ (d) all of these			(c) Ne		(d) <b>Kr</b>	
14.	The valency of inert gase	es is:		29.	The source of most of t	he n	cble gases is:	
	(a) 0	□ (b) 1			(a) decay of radioactive		•	
	(c) 2	$\Box$ (d) 3			(b) the atmospheric air			
15.		one which is non-existent:			(c) the natural gases con	ming	out of the earth	
	(a) XeF <sub>6</sub>	$\square$ (b) XeF <sub>5</sub>			(d) the decay of rocks	J		
	(c) XeF <sub>4</sub>	$\square$ (d) XeF <sub>2</sub>		l	•			

		1	•
30.	The elements with atomic numbers 10, 18, 36, 54 and 86 are		(a) $sp^3$ $\Box$ (b) $sp^2$ $\Box$
-	all:		(c) $sp^3d$ $\Box$ (d) $sp^2d$ $\Box$
	(a) light metals $\Box$ (b) inert gases $\Box$		(e) $sp^3d^2$
	(c) halogens $\Box$ (d) rare-earths $\Box$	45.	
31.	Which of the outer electronic configuration represents		(a) 107° (b) 103° (c) 119° (d) 92° (
	argon?	46.	Select the correct matching:
	(a) $ns^2$	70.	List I List II
	(c) $ns^2np^4$		A: Xe F <sub>4</sub> l. Pyramidal
32.	Which one of the following fluorides does not exist?		•
	(a) $HeF_4$ $\square$ (b) $XeF_4$ $\square$		B: Xe F <sub>6</sub> 2. T-Shape
	(c) $CF_4$ $\Box$ (d) $SF_6$ $\Box$		C: XeO <sub>3</sub> 3. Distorted octahedral
33.	Electron affinity of noble gas element is:		D: XeOF <sub>2</sub> 4. Square planar
	(a) very high	1	A B C D
-	(c) low		(a) 4
34.	In Kroll and I.C.I. process of the production of titanium, the		(b) 1 2 3 4 $\square$
	inert gas used is:		(c) 2 1 3 4
	(a) Ne		(d) 4 1 3 2 $\square$
	(c) Kr	47.	Which one of the following is a correct pair with respect to
35.	The spectrum of helium is similar to:		molecular formula of xenon compound and hybridization state
	(a) H		of xenon in it? [E.A.M.C.E.T. 2002]
	(c) $Li^+$ $\Box$ (d) $He^+$ $\Box$	1	(a) $XeF_4 sp^3$
36.	Which of the following gaseous molecules is monoatomic?		(c) $XeF_2 sp^3 d$ $\Box$ (d) $XeF_4 sp^2$ $\Box$
	(a) chlorine $\Box$ (b) helium $\Box$	48.	First compound of inert gases was prepared by Bartlett, in
	(c) oxygen $\Box$ (d) nitrogen $\Box$		1962, this compound is:
37.	Which one of the following noble gas is not found in		(a) $XeO_3$ $\Box$ (b) $XeOF_4$ $\Box$
	atmosphere?		(c) $XePtF_6$ $\Box$ (d) $XeF_6$ $\Box$
	(a) Rn	49.	
	(c) Ne $\Box$ (d) Ar $\Box$		presence of mercury vapour? [P.M.E.T. 2003]
38	Helium is added to oxygen used by deep sea divers because:		(a) XeF $\square$ (b) Xe <sub>2</sub> F $\square$ (c) XeF <sub>2</sub> $\square$ (d) XeF <sub>4</sub> $\square$
50.	(a) it is less soluble in blood than nitrogen under high	50	In $XeO_3$ and $XeF_6$ the oxidation state of $Xe$ is:
	pressure	30.	[RE.T. (M.P.) 2003]
	(b) it is lighter than nitrogen		(a) $+4 \square$ (b) $+6 \square$ (c) $+1 \square$ (d) $+3 \square$
	(c) it is readily miscible with oxygen	51	In Fischer-Ringe's method of separation of noble gas mixture
	(d) it is less poisonous than nitrogen	J1.	from air is used. [E.A.M.C.E.T. (Engg.) 2005]
30	Which of the following statements is not correct?		
3).	(a) Argon is used in electric bulbs		(a) 90% CaC <sub>2</sub> and 10% CaCl <sub>2</sub>
	(b) Krypton is obtained during radioactive disintegration □		(b) coconut charcoal
			(c) sodalime + potash solution
	(c) Half life of radon is only 3.8 days  (d) Helium is used in producing very low temperatures		(d) 90% CaCO <sub>3</sub> + 10% urea
40.		52.	Which of the following is not correct?
40.	(a) distorted octahedral $\Box$ (b) pyramidal $\Box$		[E.A.M.C.E.T. (Medical) 2005]
	_ `` • • • • • • • • • • • • • • • • • •		(a) $XeO_3$ has four $\sigma$ and four $\pi$ bonds.
41			(b) The hybridization of Xe in XeF <sub>4</sub> is $sp^3d^2$ .
41.	Which of the following exhibits the weakest inter molecular		(c) Among noble gases, the occurrence of argon is highest
	forces?		in air.
	(a) He		(d) Liquid helium is used as cryogenic liquid.
40	(c) NH <sub>3</sub> $\Box$ (d) H <sub>2</sub> O $\Box$	53.	Xenon hexafluoride reacts with silica to form a xenon
42.			compound X. The oxidation state of Xe in X is:
	about:		[E.A.M.C.E.T. (Medical) 2004; D.C.E. 2008]
	(a) 1 %		(a) $+2$ $\Box$ (b) $+4$ $\Box$ (c) $+6$ $\Box$ (d) $0$ $\Box$
40	(c) 10 %		[Hint: $SiO_2 + 2XeF_6 \longrightarrow 2XeOF_4 + SiF_4$
43.	Which of the following is planar? [C.B.S.E., P.M.T. 2000]		(X)
	(a) $XeF_4$ $\Box$ (b) $XeO_4$ $\Box$		Oxidation state of Xe in $(X)$ is $+6$ .]
	(c) $XeO_2F_2$ $\Box$ (d) $XeOF_4$ $\Box$	54.	In the Dewar's method of separation of noble gases, the
44.	The hybridization of Xe in $XeF_2$ is: [M.E.E. (Kerala) 2000]		mixture of noble gases is kept in contact with coconut

	charcoal at 173 K. Which one of the following gaseous	60.	What is the correct order of occurrence (% by weight) in	air
	mixture is not adsorbed on the charcoal?	,	of Ne, Ar and Kr? [A.F.M.C. 20	008]
	[E.A.M.C.E.T. (Engg.) 2004]		(a) Ne > Ar > Kr $\Box$ (b) Ne > Kr > Ar	
	(a) Ar, Kr		(c) $Ar > Kr > Ne$ $\Box$ (d) $Ar > Ne > Kr$	
	(c) $Xe$ , $Ar$ $\Box$ (d) $Xe$ , $Kr$ $\Box$	61.	The compound in which the number of $d\pi$ - $p\pi$ bonds	are
55.	Among the following molecules,		equal to those present in ClO <sub>4</sub> : [E.A.M.C.E.T.(Engg.) 20	
	(i) XeO <sub>3</sub> (ii) XeOF <sub>4</sub> (iii) XeF <sub>6</sub>	ļ	(a) $XeF_4$ $\Box$ (b) $XeO_3$	
	Those having same number of lone pairs on Xe are:		(c) $XeO_4$ $\Box$ (d) $XeF_6$	
	[A.I.I.M.S. 2005]	62.	The formation of $O_2^+$ [PtF <sub>6</sub> ] is the basis for the formation	n of
	(a) (i) and (ii) only $\Box$ (b) (i) and (iii) only $\Box$		xenon fluorides. This is because: [J.M.I. (Engg.) 20	
	(c) (ii) and (iii) only $\Box$ (d) (i), (ii) and (iii) $\Box$		(a) O <sub>2</sub> and Xe have comparable sizes	Ó
56.	The xenon compound(s) that are isostructural with IBr <sub>2</sub>		(b) Both O <sub>2</sub> and Xe are gases	
	and BrO <sub>3</sub> respectively are:		(c) O <sub>2</sub> and Xe have comparable ionisation energies	
	(a) linear XeF₂ and pyramidal XeO₃		(d) Both (a) and (c)	
	(b) bent XeF <sub>2</sub> and pyramidal XeO <sub>3</sub>	63.	Which of the following reactions of xenon compounds is	not
	(c) bent XeF <sub>2</sub> and planar XeO <sub>3</sub>		feasible? [A.I.E.E. 20	
	(d) linear XeF <sub>2</sub> and tetrahedral XeO <sub>3</sub>		(a) $XeO_3 + 6HF \longrightarrow XeF_6 + 3H_2O$	
	[Hint: IBr <sub>2</sub> is linear like XeF <sub>2</sub> while BrO <sub>3</sub> is pyramidal like		(b) $3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12 HF + 1.5 O_2$	
	XeO <sub>3.</sub> ]		(c) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$	
57.	Number of lone pairs of electrons on Xe atoms in XeF <sub>2</sub> , XeF <sub>4</sub>	ĺ	(d) $XeF_6 + RbF \longrightarrow Rb[XeF_7]$	
•	and XeF <sub>6</sub> molecules are respectively: [A.LE.E.E. 2002]		[Hint: The reaction (a) is not feasible because XeF <sub>6</sub> forme	d at
	(a) 3, 2 and 1 $\square$ (b) 4, 3 and 2 $\square$		once reacts with water producing again the reactants	
	(c) $2, 3$ and $1$ $\square$ (d) $3, 2$ and $0$ $\square$	64.	Argon is used: [C.E.T. (Karnataka) 20	
58.	Which is the most easily liquefiable rare gas?		(a) to obtain low temperature	
	[C.E.T. (Karnataka) 2008]		(b) in high temperature welding	
	(a) Ar		(c) in the radiotherapy for treatment of cancer	
	(c) $Xe$ $\Box$ (d) $Kr$ $\Box$		(d) in filling airships	
59	In the separation of noble gas mixture from air by Ramsay	65.	Which of the following noble gas has its ionization poten	ntial
٠,٠	Rayleigh's first method, the substances used for the removal		closest to oxygen? [C.E.C.E. (Bihar) 2	
	of $N_2$ and $O_2$ respectively, are: [P.M.E.T. 2008]		(a) He $\Box$ (b) Ne	
	(a) Cu and Mg		(c) Xe $\Box$ (d) Ar	
	(c) C and CaC <sub>2</sub> $\square$ (d) KOH solution $\square$			
G-4				
	II: This set contains the questions with two or more	correc	· · · · · · · · · · · · · · · · · · ·	
66.	XeF <sub>6</sub> on reaction with H <sub>2</sub> gives:		(a) Rare gases of atmosphere	
	(a) Xe		(b) Noble gases	
	(c) $XeF_2$ $\Box$ (d) $XeF_4$ $\Box$		(c) Inert gases	
67.	. F 1		(d) Rare-earths	
	direct reaction between the constituent elements?	70.	XeF <sub>6</sub> on hydrolysis gives:	 
	(a) $XeF_2$		(a) $XeOF_4$	
<b>4</b> 0	(c) XeOF <sub>4</sub>	71	(c) XeO <sub>3</sub>	
68.	Which of the following noble gases do not form any	71.		г
	compound? (a) He		<ul> <li>(a) XeF<sub>4</sub> and SbF<sub>5</sub> combine to form salt.</li> <li>(b) He and Ne do not form clathrates.</li> </ul>	
	(a) He		(c) He has lowest b.pt. in its group.	
69.	Which of the following names are used for group zero		(d) He diffuses through rubber and polyvinyl chloride.	
	elements?		(a) The diffuses unough tubber and poryvinyi emoride.	·I

A	nswe	rs																		
1.	(b)	2.	(c)	3.	(a)		4.	(d)	5.	(c)	6.	(d)	7.	(a)	8.	(b)	9.	(a)	10.	(c)
11.	(b)	12.	(d)	13.	(d)		14.	(a)	15.	(b)	16.	(d)	17.	(a)	18.	(b)	19.	(c)	20.	(d)
21.	(a)	22.	(c)	23.	(b)		24.	(c)	25.	(a)	26.	(c)	27.	(c)	28.	(b)	29.	(b)	30.	(b)
31.	(d)	32.	(a)	33.	(d)	`,	34.	(b)	35.	(c)	36.	(b)	37.	(a)	38.	(a)	39.	(b)	40.	(a)
41.	(a)	42.	(a)	43.	(a)		44.	(c)	45.	(b)	46.	(a)	47.	(c)	48.	(c)	49.	(c)	50.	(b)
51.	(a)	52.	(a)	53.	(c)		54.	(b)	55.	(d)	56.	(a)	57.	(a)	58.	(c)	59.	(b)	60.	(d)
61.	(c)	62.	(d)	63.	(a)		64.	(b)	65.	(c)	66.	(a, b)	67.	(c,d)	68.	(a,c)	69.	(a,b,c)	70.	(a,b,c)
71.	(a,b,c,d)																•			

## **Objective Questions for IIT ASPIRANTS**



- 1. What are the products formed in the reaction of xenon hexafluoride with silica?
  - (a) XeSiO<sub>4</sub> + HF
- (b)  $XeF_2 + SiF_4$
- (c)  $XeOF_4 + SiF_4$
- (d)  $XeO_3 + SiF_4$

[Hint:  $2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$ ]

- 2. Which of the following two are isostructural?
  - (a) XeF<sub>2</sub>, IF<sub>2</sub>
- (b) NH<sub>3</sub>, BF<sub>3</sub>
- (c)  $CO_3^{2-}$ ,  $SO_3^{2-}$
- (d) PCl<sub>5</sub>, ICl<sub>5</sub>

[Hint: XeF<sub>2</sub> is a linear molecule (Xe is  $sp^3d$  hybridized with three equatorial positions occupied by lone pairs).  $IF_2^-$  is a linear molecule (I is  $sp^3d$  hybridized, with three positions occupied by lone pairs).]

- 3. Number of atoms of He in 100 amu of He (atomic mass of He is 4) are:
  - (a)  $100 \times 6 \times 10^{23}$
- (b) 100

(c) 50

(d) 25

Mass of substance [Hint: No. of atoms = Atomic mass

- 4. The noble gas which shows abnormal behaviour in liquid state and behaves as a superfluid is:
  - (a) neon

- (b) helium
- (c) argon
- (d) xenon
- 5.  $XeF_2$  reacts with  $SbF_5$  to form:
  - (a)  $[XeF][SbF_6]$
- (b)  $[XeF_3][SbF_4]$
- (c) XeSbF<sub>6</sub>
- (d) XeF<sub>4</sub>
- Which of the following compounds is explosive?
  - (a) XeF<sub>2</sub>
- (b) XeF<sub>4</sub>
- (c) XeO<sub>3</sub>
- (d) XeF<sub>3</sub>
- 7. XeF<sub>6</sub> on reaction with CsF gives:
  - (a)  $[XeF_5][CsF_2]$
- (b) XeF<sub>8</sub>
- (c)  $[XeF_4][CsF_3]$
- (d) Cs[XeF<sub>7</sub>]
- **8.** Which of the following is/are solid at room temperature?
  - (a)  $XeF_2$

- (c) XeF<sub>6</sub>
- (b) XeF₄
- (d) All of these

## tuswers

1. (c)

2. (a)

3. (d)

5. (a)

4. (b)

**6.** (c)

7. (d)

8. (d)

# Matrix Matching Questions for IIT

#### On p-block elements

1. Match the elements of List-I with their uses in List-II:

#### List-I

#### List-II

(Element)

(Uses)

- (b) Rn
- (c) Ne

(d) Ar

- (a) He

- (p) Treatment of cancer
  - (q) Used in caution lamp
  - (r) Filled in the oxygen cylinders of sea divers
  - (s) Filled in electric bulbs
  - (t) Used in airship balloons

2. Match List-II with List-II:

#### List-I

- (a) XeF<sub>2</sub>
- (b) PCl<sub>5</sub>
- (c) XeOF<sub>4</sub> (d) XeF<sub>4</sub>
- 3. Match List-I with List-II: List-I

- (a) He (b) Xe
- (c) XeF<sub>6</sub>
- (d) IF<sub>7</sub>

- List-II
- (p) Square pyramidal
- (q) Linear shape
- (r)  $sp^3d$  hybridization
- (s)  $sp^3d^2$

#### List-II

- (p) London dispersion force
- (q) Lowest boiling noble gas
- (r)  $sp^3d^3$  hybridization
- (s) Distorted octahedral

Match the process in List-I with compounds in List-II and the 8. Match List-II with List-II: catalyst used in List-III: List-I List-II List-I List-II List-III (a) Pnicogens (p) Group-17-elements (a) Haber's process (p) Manufacture of (u) Iron powder (b) Halogens (q) Group-15-elements chlorine (r) Group-16-elements (c) Chalcogens (s) Group with solid, liquid (b) Deacon's process (q) Manufacture of (v) Pt gauge (d) Group with eight atoms nitric acid in the molecular form of and gaseous elements in free (c) Ostwald's process (r) Manufacture of (w) Copper(II) element state vanaspati ghee chloride 9. Match List-II with List-II: (d) Hydrogenation of (s) Manufacture of (x) Finely divided List-II List-I vegetable oils ammonia nickel (a) S-S linkage (p) Dithionic acid Match List-I with List-II: (b) -O-O- linkage (q) Thio-sulphuric acid List-II List-I (c)  $H_2S_2O_8$ (r) Caro's acid \_(Hybrid state-shape) (d) H<sub>2</sub>SO<sub>5</sub> (s) Marshall's acid (Compound) 10. Match List-II with List-II: (a) BCl<sub>3</sub> (p)  $sp^2$ List-I List-II (q)  $sp^3$ (b)  $H_3BO_3$ (a) Be(OH)<sub>2</sub> (p) Oxidising agent (c)  $B_2H_6$ (r) Bridge structure (b) HNO<sub>3</sub> (q) Amphoteric (d) Hybrid state of B and N (s) Triangular planar shape (c) HNO<sub>2</sub> (r) Gelatinous white ppt. in (H<sub>3</sub>NBF<sub>3</sub>) (s) Reducing agent (d)  $Al(OH)_3$ Match the halides of List-I with their properties in List-II: 11. Match each of the reactions given in column-I with corresponding List-I List-II ILLT, 20091 product(s) given in column-II: (a) BeCl<sub>2</sub> (p) Dimeric Column-I Column-II (a) Lewis Acid (b) AlCl<sub>3</sub> (a) Cu + dil. HNO3 (p) NO (r) Tetrahedral (c) CCl<sub>4</sub> (b) Cu + conc. HNO<sub>3</sub> (q) NO<sub>2</sub> (d) SiCl<sub>4</sub> (s) Pyrene (c) Zn + dil. HNO<sub>3</sub> (r)  $N_2O$ (t) Polymeric (d) Zn + conc. HNO<sub>3</sub> (s)  $Cu(NO_3)_2$ 7. Match the elements in List-I with their properties in List-II: (t)  $Zn(NO_3)_2$ List-I List-II (a)  $O_2(g)$ (p) Paramagnetic (b)  $S_2(g)$ (q) Two unpaired electrons (c) Po (r) Radioactive (d) Rn (s) Formed by α-decay of radium

## tuswers

- 1. (a-r, t)(b-p) (c-q) (d-s)7. (a-p, q) (b-p, q) (a-q, r) (b-r)(c-p, s) (d-s)(a-q) (b-p, s)(a-p, q) (b-p) (c-r, s) (d-r)(b-r, s)(a-p, q)(d-r-x)(a-s-u) (b-p-w)(c-q-v)(a-q) (b-p) 11. (a-p, s) (a-p, s) (d-q)(b-p) (c-q, r)(b-q, s)(a-t) (b-p, q) (c-r, s)(d-r)
- (d-r, s) (c-r)(c-r)(d-r)
  - (d-r)(c-s)
  - , (c-p, s) (d-q, r)
    - (d-q, t)(c-r, t)

# Assertion-Reason Type Questions

The following questions consist of two statements as Assertion (A) and Reason (R). While answering these questions, you are required to choose any one of the following responses.

- (a) If both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) If (A) is true but (R) is false.
- (d) If both (A) and (R) are false.

- 1. (A) Helium and neon do not form clathrates.
  - (R) Both have smallest atomic size among all the elements of group 18.
- 2. (A) The elements of group 18 are called inert gases.
  - (R) The elements of group 18 are mono-atomic in nature.
- 3. (A) Noble gases have highest ionisation energies in their respective periods.
  - (R) The outermost shell of the noble gases is completely filled.

- **4.** (A) Noble gases can combine with fluorine to form respective fluorides under specific conditions.
  - (R) Fluorides of He, Ar and Ne are unstable in nature.
- 5. (A) Noble gases are diamagnetic atoms.

- (R) The atomic numbers of noble gases are even and all the orbitals are doubly occupied by the electrons.
- 6. (A) He<sub>2</sub> does not exist.
  - (R) Bond order of He<sub>2</sub> is zero.

IBHU 20051



1. (a)

**2.** (b)

**3.** (c)

4. (d)

5. (a)

**6.** (a)

# THOUGHT TYPE QUESTIONS



#### THOUGHT

The noble gases have closed shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon and fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6. XeF<sub>4</sub> reacts violently with water to give XeO<sub>3</sub>. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell.

[LI.T. 2007]

- 1. Argon is used in arc welding because of its:
  - (a) low reactivity with metal
  - (b) ability to lower the melting point of metal
  - (c) flammability
  - (d) high calorific value
- 2. The structure of XeO<sub>3</sub> is:
  - (a) linear

- (b) planar
- (c) pyramidal
- (d) T-shaped
- 3.  $XeF_4$  and  $XeF_6$  are expected to be:
  - (a) oxidising
- (b) reducing
- (c) unreactive
- (d) strongly basic



Thought 1

1. (a)

2. (c)

3. (a)

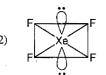
# INTEGER ANSWER THE Constitute

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. How many noble gases are radioactive in nature?
- 2. What is the bond order of Ne<sub>2</sub>?
- 3. What is the percentage by volume of inert gases in the atmosphere?
- **4.** How many lone pairs of electrons are present on xenon atom in  $XeF_4$ ?
- **5.** Xenon hexafluoride reacts with silica. What is the oxidation state of xenon in the xenon compound formed?

## Auswers

- 1. (2) Radon and ununoctium.
- 2. (0) Number of bonding and antibonding electrons are equal.
- **3.** (1)



5. (6)  $2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$ 

# Revision Exercise (Chapter 8 to 13)

	J

SIN	GLE CORRECT ANSWER TYPE		9.	The ease of liquefaction of noble gases decreases the order	:
1	Which of the following oxides of nitrogen is paramagnet	io?		(a) $He > Ne > Ar > Kr > Xe$	ļ
1.	(a) $N_2O$ $\square$ (b) $N_2O_5$			(b) $Xe > Kr > Ar > Ne > He$	
		_		(c) $Kr > Xe > He > Ar > Ne$	]
2	(c) $NO_2$ $\Box$ (d) $N_2O_3$			(d) $Ar > Kr > Xe > He > Ne$	□ .
2.	The major role of fluorspar (CaF <sub>2</sub> ) which is added in sn		10.	Al and Ga have nearly same covalent radius because of:	
	quantity in the electrolytic reduction of alumina dissolved	ı ın		•	
	eryolite (Na <sub>3</sub> AlF <sub>6</sub> ) is:			- · · · -	
	(i) as a catalyst				
	(ii) to make the mixture very conducting				
	(iii) to lower the temperature of the melt		11.	Ge(II) compounds are powerful reducing agents wherea	is
	(iv) to decrease the rate of oxidation of carbon at anode			Pb(IV) compounds are strong oxidising agents. It can be du	
	Correct option is:			to:	
	(a) (i), (ii)				_
_	(c) (i), (ii), (iii)				_
3,	Which one of the following compounds has the smal	lest		(c) ionic radii of Pb <sup>2+</sup> and Pb <sup>4+</sup> are larger than those of Ge <sup>2</sup>	
	bond angle in the molecule?			4+	
	(a) $SO_2$			(d) more pronounced inert pair effect in lead than in Ge I	
	(c) $H_2S$ $\square$ (d) $NH_3$		12	Which of the following statements is incorrect?	_
4.	Thallium shows different oxidation states because:		12.	(a) ICl is a good conductor of electricity in fused state. I	٦
	(a) of its reactivity				_
	(b) of its amphoteric nature			(c) Melting and boiling points of HBr are more than HCl.!	
	(c) it is a transition metal				_
	(d) of inert pair effect of electrons		13	Amorphous boron is extracted from borax by following steps	
5.	Match list-I with list-II and select the correct answer:		15.	Timosphous boson is extracted from bostax by somewing steps	,.
	List-I List-II			Borax $\xrightarrow{(A)}$ H <sub>3</sub> BO <sub>3</sub> $\xrightarrow{(B)}$ B <sub>2</sub> O <sub>3</sub> $\xrightarrow{(C)}$ Boron	
	(p) XeF <sub>4</sub> 1. Distorted octahedral			(A) and (C) are :	
	(q) XeF <sub>6</sub> 2. Tetrahedral			/	
	(r) XeO <sub>3</sub> 3. Square planar		i i		
	(s) XeO <sub>4</sub> 4. Pyramidal			$(c) Hel, re \qquad (d) H2SO4, Na$	
	(a) $p-3$ , $q-1$ , $r-4$ , $s-2$ $\Box$ (b) $p-2$ , $q-3$ , $r-1$ , $s-4$		14.	In the process $XH_3 + H^+ \longrightarrow XH_4^+$ (X being N, P, As	or
	(c) $p-4$ , $q-1$ , $r-3$ , $s-2$ $\square$ (d) $p-1$ , $q-4$ , $r-2$ , $s-3$			Sb), the maximum increase in the bond angle will be in the	ıe
6.	Which of the following represents the correct order	of		case of:	
	decreasing number of $S = O$ or $S \to O$ bonds?			(a) $NH_3$ $\square$ (b) $PH_3$	
	(a) $H_2S_2O_8 > H_2SO_4 > H_2SO_3$			(c) $AsH_3$ $\Box$ (d) $SbH_3$	
	(b) $H_2SO_3 > H_2S_2O_8 > H_2SO_4$		15.	When Cl <sub>2</sub> water is added to an aqueous solution	of
	(c) $H_2S_2O_8 > H_2SO_3 > H_2SO_4$			potassium iodide in presence of chloroform, a violet color	
	(d) $H_2SO_4 > H_2SO_3 > H_2S_2O_8$			is obtained. On adding more of Cl <sub>2</sub> water, the violet color	
7.	The heavier elements of group 15 do not form $p\pi$ - $p\pi$ be	nds		disappears. This is due to formation of:	
	because:				
	(a) their atomic orbitals are large and diffused			· · · · · · · · · · · · · · · · · · ·	
	(b) their atomic orbitals do not overlap effectively	. 🗆	16.	Hydrolysis of PI <sub>3</sub> yields:	
	(c) both (a) and (b) $\square$ (d) none of these				
8.	Bones glow in dark. This is due to:				
	(a) conversion of white P into red P			* *	
	(b) conversion of red P into white P				
	(c) slow combustion of white P in contact with air		17.	In $[B_4O_5(OH)_4]^{2-}$ , the number of boron atoms having an oct	
	(d) none of the above			of electrons is:	

	(c) 2	☐ (b) 1 ☐ (d) 4			SWERS TYPE
18.	$B_2H_6 \xrightarrow{\text{excess NH}_3} A, A \text{ is}$	s:		31.	Which of the following statements are correct?
		$\Box$ (b) B <sub>2</sub> H <sub>6</sub> ·2NH <sub>3</sub>			(a) Conc. HNO <sub>3</sub> attacks Al liberating NO <sub>2</sub> .
		$\square  \text{(d) all of these}$			(b) Al dissolves in HCl and not in conc. NaOH.
10		on while SiO is unstable beca	_		(c) The corrosion of Al is prevented by the formation of a
17.	(a) carbon can form coor				coating of its oxide on its surface.
	• •	t between C and O which is			(d) Dilute H <sub>2</sub> SO <sub>4</sub> attacks Al very slowly evolving hydrogen.
	possible in SiO	t between e and e when h			
	(c) carbon is smaller in si	ze than silicon		32.	Mark the correct statements:
	(d) none of the above	ze than sincon			(a) Alumina is used as a refractory material.
20	The chain building unit in	silicone nolymer is :			(b) Boron carbide is used as an abrasive for polishing. □
	, -	☐ (b) MeSiCl <sub>3</sub>			(c) Borax is used in glazing.
		☐ (d) none of these			(d) Alum is used for fire-proofing fabrics. $\Box$
21	Equimolar mixture of PCl	• •	·		Graphite:
<b>~</b> 1.	(a) POCl <sub>3</sub>	☐ (b) H <sub>3</sub> PO <sub>3</sub>			(a) is paramagnetic □ (b) has unpaired electrons □
		☐ (d) both (a) and (c)			(c) has mobile electrons □ (d) is diamagnetic □
22	The hybridisation of P in			34.	Mark the incorrect statements:
LL.		$\Box$ (b) S in SO <sub>3</sub>			(a) Silicon hydrides are known as silicones.
	(c) N in NO <sub>3</sub>				(b) Liquid silicones act as lubricants.
22		•			(c) Sheet silicates are formed from [SiO <sub>4</sub> ] <sup>4</sup> tetrahedral units
23.		s used in lead storage batteric powerful oxidising agent, is:	28, III		by sharing three oxygen atoms.
	•				(d) Buckminsterfullerene is paramagnetic as it has unpaired
	(a) PbO <sub>2</sub>	☐ (b) Pb <sub>3</sub> O <sub>4</sub> ☐ (d) 2PbO·PbO <sub>2</sub>		25	electrons.
24	(c) PbO The order of hand langth	in NO, NO $_3$ , NO $_2$ and N $_2$ O $_4$	 :a.:	33.	$(NH_4)_2Cr_2O_7$ on heating gives :
<i>2</i> 4,					(a) $Cr_2O_3$ $\square$ (b) $N_2$ $\square$ (c) $NO$ $\square$ (d) $NH_3$ $\square$
•	(a) $NO_3^- > NO_2^- > N_2O_4$			36	Which acids are formed by the action of water on phos-
	(b) $NO > N_2O_4 > NO_2^- >$			50.	phorus pentoxide?
	(c) $NO > NO_3^- > N_2O_4 >$	_			(a) $HPO_3$ $\Box$ (b) $H_4P_2O_7$
	(d) $N_2O_4 > NO_2^- > NO_3^-$	> NO			(c) $H_3PO_4$ $\Box$ (d) $H_3PO_3$ $\Box$
25.	Oxygen is more electroneg	gative than sulphur. Yet $H_2S$ is a	cidic	37.	HI can not be prepared by heating KI with conc. H <sub>2</sub> SO <sub>4</sub>
	while H <sub>2</sub> O is neutral. Thi	s is due to:			because :
	(a) H <sub>2</sub> S is a gas while H <sub>2</sub>	O is a liquid			(a) H <sub>2</sub> SO <sub>4</sub> is stronger than HI
	(b) H—S bond is weaker				(b) HI is stronger than H <sub>2</sub> SO <sub>4</sub> □
	(c) H <sub>2</sub> O is highly associa	-			(c) H <sub>2</sub> SO <sub>4</sub> is an oxidising agent □
	(d) molecular mass of H <sub>2</sub>	$_{2}S$ is more than that of $H_{2}O$			(d) HI is a reducing agent
26.	In ozone, there are:			38.	Mark out the incorrect match of shape:
	(a) $2\sigma$ and $1\pi$ bonds	$\Box$ (b) $1\sigma$ and $2\pi$ bonds			(a) ICl <sub>4</sub> : Square planar □ (b) XeOF <sub>2</sub> : Trigonal planar □
	(c) $2\sigma$ and $2\pi$ bonds				(c) $[SbF_5]^{2-}$ : Square bipyramidal
		l one lone pair of electrons			(d) $NH_2$ : Pyramidal
27.	Which of the following l	halogens is called super halog	gen?	39.	Select the correct order of reactivity:
	(a) Fluorine	☐ (b) Chlorine			(a) $HI>HBr>HCI>HF$ $\Box$ (b) $HCIO_4>HBrO_4>HIO_4$ $\Box$
	(c) Bromine	☐ (d) Iodine			(c) HClO <hbro<hio< td=""></hbro<hio<>
28.	0.1	nfected by bubbling through	water		(d) HClO <sub>4</sub> >HClO <sub>3</sub> >HClO <sub>2</sub> >HClO
	a controlled quantity of:			40.	Which of the following statements are correct?
	(a) $Br_2$	□ (b) N <sub>2</sub>			(a) Cl <sub>2</sub> reacts with aqueous Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> to form HCl and
	(c) Cl <sub>2</sub>	$\square$ (d) $O_2$			NaHSO <sub>4</sub> .
29.	Diamagnetic oxide of chl				(b) Cl <sub>2</sub> reacts with aqueous Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> to give Na <sub>2</sub> S <sub>4</sub> O <sub>6</sub> and
	(a) ClO <sub>2</sub>	☐ (b) ClO <sub>3</sub>			NaCl.
	(c) Cl <sub>2</sub> O <sub>6</sub>	$\Box$ (d) none of these			(c) A white precipitate of silver thiosulphate is formed which
30.	The reaction of XeF <sub>6</sub> wit	-			changes to yellow, brown and finally black when silver nitrate is added to $Na_2S_2O_3$ .
	(a) XeF <sub>4</sub> and SiF <sub>4</sub>	$\Box$ (b) XeOF <sub>2</sub> and SiF <sub>4</sub>			(d) Sodium thiosulphate is quantitatively oxidised by iodine.
	(c) XeOF <sub>4</sub> and SiF <sub>4</sub>	☐ (d) none of these			(a) Sociali anosaiphae is quantitatively oxidised by founde.

#### ASSERTION-REASON TYPE QUESTIONS

The questions given below consist of an Assertion (A) and Reason (R). Use the following key for the appropriate answer of each question.

- (a) Both (A) and (R) are correct and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are correct but (R) is not the correct explanation of (A).
- (c) (A) is correct but (R) is incorrect.
- (d) (A) is incorrect but (R) is correct.
- (e) Both (A) and (R) are incorrect.
- 41. (A) Lead exhibits oxidation states of +2 and +4.
  - (R) Lead exhibits inert pair effect.
- **42.** (A) Al forms  $[AlF_6]^{3-}$  but B does not form  $[BF_6]^{3-}$ .
  - (R) B does not react with fluorine.
- 43. (A) PF<sub>5</sub> and IF<sub>5</sub> have similar shapes.
  - (R) PF<sub>5</sub> has two types of P—F bond lengths.
- **44.** (A) Xenon forms three fluorides with molecular formulae XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub>.
  - **(R)** The formation of xenon fluorides involves the unpairing of *p*-orbitals and promotion of electron or electrons to the vacant *d*-orbitals in the outermost shell. The number of unpaired orbitals under the excited states are either 2 or 4 or 6.
- **45.** (A) Halogens combine with each other and form binary covalent compounds of  $AB_n$  type which are called interhalogen compounds. B is always smaller atom and n may have values 1 to 7.
  - (R) Interhalogen compounds are less reactive than  $A_2$  or  $B_2$  molecules.
- **46.** (A) Sulphuric acid has great affinity for water. It acts as a powerful dehydrating agent.
  - (R) Sulphuric acid has corrosive action on skin also.
- **47.** (A) Boron, aluminium and gallium form complex anionic hydrides of the type NaBH<sub>4</sub>, LiAlH<sub>4</sub> and LiGaH<sub>4</sub>, respectively.
  - (R) These complex hydrides are powerful reducing agents.
- **48.** (A) The abundance of carbon is more than silicon in earth's crust.
  - (R) Carbon has the maximum property of catenation.
- **49.** (A) All the oxidation states of nitrogen from +1 to +4 show disproportionation in acidic medium.
  - (R) Aqueous nitric acid undergoes disproportionation.
- **50.** (A) All the halogens are paramagnetic in atomic forms.
  - (R) Halogens have seven electrons in their outermost shell *i.e.*, they have  $ns^2np^5$  configuration.

#### MATRIX MATCHING QUESTIONS

51. Match Column-II with Column-III:

Column-I	Column-II	Column-III
(a) XeF <sub>2</sub>	(p) 90°	(i) Tetrahedral
(b) XeF <sub>4</sub>	(q) 109.5°	(ii) Pyramidal
(c) XeO <sub>4</sub>	(r) 103°	(iii) Linear
(d) XeO <sub>3</sub>	(s) 180°	(iv) Square planar

52. Match Column-I with Column-II:

Column-I	Column-II		
(a) $H_3PO_2$	(p) Reducing		
(b) $H_2S$	(q) Monobasic		
(c) HNO <sub>2</sub>	(r) Dibasic		
(d) HI	(s) Oxidising		

53. Match Column-I with Column-II:

Tracen Column 1 with Column 11:	
Column-I	Column-II
(a) $Zn + V$ . dil. $HNO_3$	(p) NO
(b) $Sn + dil. HNO_3$	(q) NO <sub>2</sub>
(c) $Ag + dil. HNO_3$	(r) $NH_4NO_3$
(d) Pb + conc. HNO <sub>3</sub>	(s) $Sn(NO_3)_2$
	(t) $Zn(NO_3)_2$

54. Match Column-I with Column-II:

Column-I	Column-II
(a) $NH_4NO_3$	(p) Laboratory reagent
(b) $(NH_4)_2SO_4$	(q) In making dry cells
(c) NH <sub>4</sub> Cl	(r) Fertiliser
(d) NH <sub>4</sub> OH	(s) Explosive

55. Match Column-I with Column-II:

Column-I	Column-II		
(a) $P_4O_{10}$	(p) Ionic		
(b) SiO <sub>2</sub>	(q) Covalent		
(c) $Al_2O_3$	(r) Acidic		
(d) SnO	(s) Amphoteric		

**56.** Match Column-I with Column-II:

Column-1	Column-II
(a) HF	(p) Reducing agent
(b) HI	(q) Oxidising agent
(c) Cl <sub>2</sub>	(r) Precipitate with AgNO <sub>3</sub> solution
(d) (CN) <sub>2</sub>	(s) Attacks glass
	(t) Pseudo halogen

#### LINKED COMPREHENSION TYPE

#### Passage 1

Silicates are minerals containing tetrahedral SiO<sub>4</sub><sup>4</sup> structural units. A variety of silicate structures occur in nature, ranging from single tetrahedra to pairs, rings, chains, sheets and three-dimensional networks of linked tetrahedra with cations to balance the total charge in the crystal. In aluminosilicates, aluminium atoms substitute for some of tetrahedrally bonded silicon atoms and additional cations are present in order to maintain a net charge of zero. Zeolites are network aluminosilicates having pores on a molecular scale. They are useful for exchanging ions, for separating mixtures of gases and as catalysts.

Answer the following questions:

- 57. Silicates which contain two units of SiO<sub>4</sub><sup>4</sup> joined along a corner containing oxygen are called:
  - (a) orthosilicates(b) pyrosilicates(c) cyclic silicates(d) chain silicates

- 58. The general formula of cyclic or ring silicates is:
  - (a)  $(Si_2O_5)_n^{2n}$
- (b)  $(SiO_3)_n^{2n-}$
- (c)  $(SiO_3^2)_n$
- (d) both (b) and (c)
- 59. Mark the incorrect statement:
  - (a) Zeolites are a class of three dimensional aluminosilicates which can accommodate water molecules in their cavities.
  - (b) Quartz, tridymite, feldspar, etc. are three dimensional silicates.
  - (c) Zeolites can be used to soften hard water.
  - (d) Three dimensional silicates involve three oxygen atoms of each tetrahedra for sharing with adjacent tetrahedra.

#### Passage 2

All the elements of group 13 form trihalides. The boron halides are covalent. The trifluorides of Al, Ga, In and Tl are ionic while chlorides, bromides and iodides are largely covalent when anhydrous. However, their covalent nature decreases on moving from Ga to Tl. Trihalides fume in air and undergo hydrolysis. They act as Lewis acids. They form complex halides.

Answer the following questions:

- 60. Which of the halides does not undergo hydrolysis?
  - (a) BF<sub>3</sub>

(b) BCl<sub>3</sub>

(c) AlF<sub>3</sub>

- (d) AlCl<sub>3</sub>
- **61.** Which of the following statements about anhydrous aluminium chloride is correct?
  - (a) It exists as AlCl<sub>3</sub> molecule.
  - (b) It is not easily hydrolysed.
  - (c) It sublimes at 100°C under vacuum.
  - (d) It is a strong Lewis base.
- **62.** Which of the following statements is correct?
  - (a) Both AlCl<sub>3</sub> and BCl<sub>3</sub> are not Lewis acids.
  - (b) Both AlCl<sub>3</sub> and BCl<sub>3</sub> are equally strong Lewis acids.
  - (c) AlCl<sub>3</sub> is stronger Lewis acid than BCl<sub>3</sub>.
  - (d) BCl<sub>3</sub> is stronger Lewis acid than AlCl<sub>3</sub>.

#### Passage 3

The chemistry of fluorine differs sharply from the other halogens. Fluorine atoms form weak bonds to other fluorine atoms but particularly strong bonds to most other kinds of atoms. Fluorine displaces other halogens from their compounds and oxidises elements in compounds exposed to it. The compounds of fluorine with metals in their lower oxidation states are salts with strong ionic character. The higher oxidation states of many of the

same elements yield volatile fluorides with significant covalent character.

Compounds of fluorine with the non-metals possess a wide range of reactivities and molecular geometries. SF<sub>6</sub> is an inert compound while BF<sub>3</sub> is a strong lewis acid. SbF<sub>5</sub> is a strong fluorinating agent. PtF<sub>6</sub>, a strong fluorinating agent has opened up modern research on the compounds of the noble gases.

Answer the following questions:

- **63.** Which can bring the highest oxidation state in the transition metal?
  - (a)  $F_2$

(b) Cl<sub>2</sub>

(c) Br<sub>2</sub>

- (d) I<sub>2</sub>
- **64.** Among the fluorides given below which will further react with F<sub>2</sub>:
  - (a) NaF

(b) CaF<sub>2</sub>

(c) SF<sub>6</sub>

- (d)  $\mathbf{IF}_5$
- 65. Which one of the following reactions does not occur?
  - (a)  $F_2 + 2Cl^- \longrightarrow 2F^- + Cl_2$
  - (b)  $Cl_2 + 2F^- \longrightarrow 2Cl^- + F_2$
  - (c)  $Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$
  - (d)  $F_2 + 2Br^- \longrightarrow 2F^- + Br_2$

#### **INTEGER ANSWER TYPE**

- **66.** How many  $\pi$ -bonds are present in the molecule of borazine?
- **67.** The number of isomers possible for disubstituted borazine,  $B_3N_3H_4X_2$  is:
- **68.** Red lead reacts with conc. HCl according to following reaction,

$$Pb_3O_4 + HCl \longrightarrow XPbCl_2 + Cl_2 + H_2O$$

Balance this reaction and find the value of X.

- 69. What is the basicity of phosphorus acid?
- **70.** How many sigma bonds are present in the molecule of caro's acid?
- 71. What is the oxidation state of S in  $H_2SO_4$ ?
- **72.** How many lone pairs of electrons are present in central atom of ClF<sub>3</sub>?

# Answers with Hints

- 1. (c) NO<sub>2</sub> is paramagnetic due to the presence of unpaired electron.
- 2. (b) CaF<sub>2</sub> in the system acts as a thinner. It lowers the temperature of the melt and makes it more conducting.
- 3. (c)  $SO_2$   $H_2O$   $H_2S$   $NH_3$   $sp^2$   $sp^3$   $sp^3$   $sp^3$   $sp^3$  119.5° 104.5° 92.5° 107.5°
- 4. (d)
  5. (a)  $XeF_4$   $sp^3d^2$  Square planar  $XeF_6$   $sp^3d^3$  Distorted octahedral  $XeO_3$   $sp^3$  Pyramidal
- $XeO_3$   $sp^3$  Pyramidal  $XeO_4$   $sp^3$  Tetrahedral

(One S=O bond)

- **7.** (c)
- 8. (c) 4P + 5O<sub>2</sub> → P<sub>4</sub>O<sub>10</sub> + light

  The phenomenon of emitting light as a result of chemical change is called chemiluminescence.
- 9. (b) Ease of liquefaction increases in the group from top to bottom as van der Waals' forces increase with increase of atomic size.
- **10.** (b) Due to poor shielding effect of *d*-electrons the outer electrons in Ga experience more attraction by the nucleus.
- 11. (d) Ge(IV) is more stable than Ge(II) while Pb(II) is more stable than Pb(IV).
- 12. (d) Fluorine does not form oxoacid.
- 13. (d)  $Na_2B_4O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2B_4O_7$

$$H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3$$
  
 $2H_3BO_3 \xrightarrow{\text{Heat}} B_2O_3 + 3H_2O$   
 $B_2O_3 + 6Na \longrightarrow 2B + 3Na_2O$ 

14. (d) The bond angle in the hydrides vary in the order :

$$NH_3 > PH_3 > AsH_3 > SbH_3$$

In the formation of  $XH_4^+$ , the bond angle becomes  $109^{\circ}28'$  Hence maximum increase will occur in SbH<sub>3</sub>.

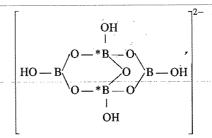
15. (c) 
$$2KI + Cl_2 \longrightarrow 2KCI + I_2$$

$$I_2 + CHCl_3 \longrightarrow Violet layer$$

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

$$I_2 + H_2O + 5[O] \longrightarrow 2HIO_3$$

- 16. (b)  $PI_3 + 3H_2O \longrightarrow 3HI + H_3PO_3$ (Monobasic) (Dibasic)
- 17. (c) Borax ion can be represented as:



Thus, borax contains two B-atoms having an octet of electrons.

18. (a) 
$$B_2H_6 + NH_3 \longrightarrow B_2H_6 \cdot 2NH_3$$

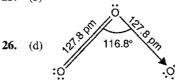
$$High temp. (BN)_x$$

$$B_2H_6 \cdot 2NH_3 \xrightarrow{High} B_3N_3H_6$$

- **19.** (b)
- **20.** (c)

21. (a) 
$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$
  
 $(1 : 1)$   $PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$   
 $(1 : 4)$ 

- **22.** (d)  $ICl_{4}^{-}$   $SO_{3}$   $NO_{3}^{-}$   $SO_{4}^{2-}$   $PO_{4}^{3-}$   $sp^{3}$   $sp^{3}$   $sp^{3}$
- **23.** (a)
- 24. (a) NO  $N_2O_4$  NO $_3^-$  NO $_2^-$ Bond length 115 pm 117 pm 122 pm 121 pm
- **25.** (b)



- 27. (a) 28. (c) 29. (c)
- 30. (c)  $2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$
- **31.** (c, d)
- 32. (a, b, c)
- 33. (c, d) Graphite has sigma and  $\pi$ -bonds. The  $\pi$ -electrons are free to move throughout the entire layers.
- **34.** (a, d) Silicon hydrides are known as silanes. Buckminsterfullerene is diamagnetic as it does not have unpaired electrons.
- 35. (a, b)  $(NH_4)_2Cr_2O_7 \xrightarrow{\text{heat}} N_2 + Cr_2O_3 + 4H_2O_3$

36. (a, b, c) 
$$P_4O_{10} \xrightarrow{2H_2O} 4HPO_3 \xrightarrow{2H_2O} 2H_4P_2O_7$$

Metaphosphoric acid

$$4H_3PO_4 \xleftarrow{2H_2O}$$
Orthophosphoric

37. (c, d) 
$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$
Reducing Oxidising agent

38. (b, d) 
$$XeOF_2 - sp^3d \longrightarrow T$$
-shaped  $NH_2^- - sp^3 \longrightarrow V$ -shaped

**40.** (a, c, d) 
$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$$
  
 $2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$   
 $Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$   
 $2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$ 

**41.** (a)

**42.** (c) B does not have d-orbitals.

43. (d) PF<sub>5</sub> has trigonal bipyramidal shape having two types of P—F bond lengths.
IF<sub>5</sub> has square pyramidal shape.

**44.** (a)

**45.** (e) Assertion is wrong as n may have values 1, 3, 5 and 7. Reason is also wrong as interhalogen compounds are more reactive than  $A_2$  or  $B_2$  molecules as A—B bond is weaker than A—A and B—B bonds.

**46.** (b)

**47.** (b)

**48.** (d) Carbon is less abundant than silicon in the earth's crust, however, compounds of carbon are very large due to catenation property.

**49.** (c) (A) is correct while (R) is incorrect. In HNO<sub>3</sub>, the oxidation state of nitrogen is +5.

**50.** (a)

**51.** (a-s-iii); (b-p-iv); (c-q-i); (d-r-ii)

**52.** (a-p, q); (b-p, r); (c-p, q, s); (d-p, q)

53. (a-r, t); (b-r, s); (c-p); (d-q)

**54.** (a-r, s); (b-p, r); (c-p, q); (d-p)

**55.** (a-q, r); (b-q, r); (c-p, s); (d-p, s)

**56.** (a-s); (b-p, r); (c-q); (d-q, t)

**57.** (b)

58. (d)

**59.** (d)

60. (a) BF<sub>3</sub> forms an addition product with water as B—F bond is very strong.

$$BF_3 + H_2O \Longrightarrow H^+[BF_3OH]$$

**61.** (c)

**62.** (d)

**63.** (a)

**64.** (d)  $IF_5 + F_2 \longrightarrow IF_7$ 

65. (b)

66. Three: Borazine has structure similar to benzene.

67. Four: See objective question 15 on Page 407.

**68.** Three:  $Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + Cl_2 + 4H_2O$ 

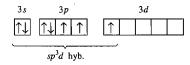
69. Two: H<sub>3</sub>PO<sub>3</sub> is a dibasic acid. It forms two series of salts.

**70.** Seven:  $H_2SO_5$  is represented as:

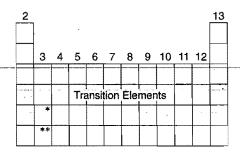
$$\begin{array}{c} O \\ H \xrightarrow{\sigma} O \xrightarrow{\sigma \parallel} S \xrightarrow{\sigma} O \xrightarrow{\sigma} O \xrightarrow{\sigma} H \\ O \end{array}$$

**71.** Six

72. Two: Cl in first excited state



# CHAPTER 14



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# Transition Elements or d-block Elements and f-block Elements

## 14.1 INTRODUCTION

In the extended form of the periodic table, the elements have been grouped into four blocks namely s, p, d and f-blocks. The elements belonging to groups 3 to 12 are called **d-block** or **transition elements**. These are present between s-block and p-block elements. The properties of these elements are intermediate between the properties of s-block and p-block elements, i.e., d-block elements represent change or transition in properties from most electropositive s-block elements to least electropositive p-block elements. Therefore, these elements are called **transition elements**.

Previously the transition elements were regarded as those elements which possessed partially filled penultimate d-subshells in their ground state or in one of their commonly occurring oxidation states. This definition included coinage metals (Cu, Ag and Au) in the transition elements as their ions have partially filled (n-1)d-subshells although their atoms have filled (n-1)d-subshells in the ground state.

Cu	$3d^{10}4s^1$	Cu <sup>2+</sup>	$3d^{9}$
Ag	$4d^{10}5s^1$	Ag <sup>2+</sup>	$4d^9$
An	$5d^{10}6s^1$	Au <sup>3+</sup>	$4d^8$

However, the above definition does not cover the elements of group 12, *i.e.*, zinc metals (Zn, Cd and Hg) as these elements do not have partially filled (n-1)d-subshells either in the ground state or in ions.

Zn	$3d^{10}4s^2$	$Zn^{2+}$	$3d^{10}$
Cd	$4d^{10}5s^2$	Cd <sup>2+</sup>	$4d^{10}$
Hg	$5d^{10}6s^2$	Hg <sup>2+</sup>	$5d^{10}$

However, zinc metals showing similarities in some of chemical properties with transition metals are also included in this block. These are considered as end members of the transition series in order to maintain a rational classification of elements.

Forty elements belong to *d*-block. Fourth, fifth, sixth and seventh periods consist of ten elements each.

	]	d-block Transition elements									
	III B	IV B	V B 5	VI B	VII B 7	8	VIII 9	10	I B 11	II B 12	
	21 Sc	22 <b>T</b> i	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	
s-block	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	p-block
	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	
;	89 Ac	104 Ku	105 Ha	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	

The *d*-block elements include the most common metal used in construction and manufacturing (iron), metals that are valued for their beauty (gold, silver and platinum), metals used in coins (nickel, copper) and metals used in modern technology (titanium). Copper, silver, gold and iron were known and used in early civilization. This group contains the densest elements (osmium,  $d = 22.59 \text{ g cm}^{-3}$  and iridium,  $d = 22.61 \text{ g cm}^{-3}$ ), the metals with the highest and lowest melting points (tungsten, m.p. =  $3410^{\circ}$ C and mercury, m.p. =  $-38.9^{\circ}$ C) and radioactive elements such as technetium and ten members of seventh period.

Certain d-block elements are particularly important in living organisms. Iron, the transition element, is present in the largest quantity in the human body. The best known biological ironcontaining compound is the protein haemoglobin, the red component of blood that is responsible for the transport of oxygen. Cobalt is the crucial element in vitamin B<sub>12</sub>, a compound that acts as a catalyst in the metabolism of carbohydrates, fats and proteins. Molybdenum and iron together with sulphur form the reactive portion of nitrogenase, a biological catalyst used by nitrogen fixing organisms to convert atmospheric nitrogen into ammonia. Copper and zinc are important in other biological catalysts. Iron, zinc, copper, cobalt, nickel, manganese and molybdenum are known to be essential components of enzymes. Vanadium and chromium are also essential for life. Some bad elements are also present in this block. For example, mercury is toxic and is threat to the environment.

## 14.2 ELECTRONIC CONFIGURATION

In the transition elements, the last differentiating electron is accommodated on penultimate *d*-orbitals, *i.e.*, *d*-orbitals are successively filled. The general electronic configuration of transition elements is:

$$(n-1)d^{1-10} ns^{0,1 \text{ or } 2}$$

There are four complete rows (called series) of ten elements each corresponding to filling of 3d, 4d, 5d and 6d-orbitals respectively. Each series starts with a member of group third (IIIB) and ends with a member of group twelve (IIB).

**First transition or** 3d**-sc ies :** This series consists of elements from Sc(21) to Zn(30). 3d-orbitals are gradually filled up.

Element	Symbol	At. No.	•	Electronic configuration
Scandium	Sc	21		$1s^2$ , $2s^22p^6$ , $3s^23p^63d^1$ , $4s^2$
			_	or [Ar] $3d^{1}4s^{2}$
Titanium	Ti	22	ď.	[Ar] $3d^24s^2$
Vanadium	V	- 23	filled	$[Ar] 3d^34s^2$
Chromium	Cr*	24		[Ar] $3d^54s^1$
Manganese	Mn	25	are	[Ar] $3d^54s^2$
Iron	Fe ·	26	tals	$-[Ar] 3d^64s^2$
Cobalt	Co	27	3d-orbitals	[Ar] $3d^{7}4s^{2}$
Nickel	Ni	28	-pg	[Ar] $3d^84s^2$
Copper	Cu*	29		[Ar] $3d^{10}4s^1$
Zinc	Zn	30	4	[Ar] $3d^{10}4s^2$

The configuration of Cr and Cu are different than expected. The actual configurations are explained on the basis of stability concept of half-filled or completely filled (n-1)d-orbitals. (n-1)d-subshell is more stable when 5 or 10 electrons are present, *i.e.*, every d-orbital is either singly occupied or doubly occupied.

**Second transition or 4***d***-series :** This series consists of elements from Y(39) to Cd(48). 4*d*-orbitals are gradually filled up.

Element	Symbol	At. No.	Electronic configuration
Yttrium	Y	39	[Kr] $4d^1 5s^2$
Zirconium	Zr	40	[Kr] $4d^2 5s^2$
Niobium	${ m Nb}^*$	41 🚊	[Kr] $4d^4 5s^1$
Molybdenum	Mo <sup>*</sup>	42	[Kr] $4d^5 5s^1$
Technetium	Tc*	42 de lilled	[Kr] $4d^6 5s^2$
Ruthenium	Ru*	1 /1/1 1	$[Kr] 4d^7 5s^1$
Rhodium	Rh*	45 46 47 44-orbitals	[Kr] $4d^8 5s^1$
Palladium	Pd*	46 7	[Kr] $4d^{10} 5s^0$
Silver	Ag*	47 7	[Kr] $4d^{10} 5s^1$
Cadmium	Cd	48	[Kr] $4d^{10} 5s^2$

Elements marked with asterisk have anomalous configurations. These are attributed to factors like nuclear-electron and electron-electron forces.

**Third transition or 5***d***-series:** This series consists of elements from La(57) to Hg(80) except 14 elements of lanthanide series from Ce(58) to Lu(71). 5*d*-orbitals are gradually filled up.

Element	Symbol	At. No.	Electronic configuration
Lanthanum	La	57	[Xe] $5d^1 6s^2$
Hafnium	Hf	72 g	[Xe] $4f^{14} 5d^2 6s^2$
Tantalum	Ta	73 👨	[Xe] $4f^{14} 5d^3 6s^2$
Tungsten	w	74 👸	[Xe] $4f^{14} 5d^4 6s^2$
Rhenium	Re	75 eg	[Xe] $4f^{14} 5d^5 6s^2$
Osmium	Os	1 7/	[Xe] $4f^{14} 5d^6 6s^2$
Iridium	Ir	76 77 78 79 79 79 79 79 79 79 79 79 79 79 79 79	[Xe] $4f^{14} 5d^7 6s^2$
Platinum	Pt*	78 💆	[Xe] $4f^{14} 5d^9 6s^1$
Gold	Au*	79 5	[Xe] $4f^{14} 5d^{10} 6s^1$
Mercury	Hg	80	[Xe] $4f^{14} 5d^{10} 6s^2$

**Fourth transition or 6d-series:** This series consists of elements from Ac(89) to Uub(112) except 14 elements of actinide series from Th(90) to Lr(103). 6d-orbitals are gradually filled up.

	•		
Element	Symbol	At. No.	Electronic configuration
Actinium	Ac	89	[Rn] $6d^1 \overline{7s^2}$
Rutherfordium	Rf	104	[Rn] $5f^{14} 6d^2 7s^2$
Hahnium	Ha	105	$  \cdot [\text{Rn}]  5f^{14}  6d^3  7s^2$
Seaborgium	Sgt	106	[Rn] $5f^{14} 6d^4 7s^2$
Bohrium	Bh†	107	[Rn] $5f^{14} 6d^5 7s^2$
Hassium	Hs†	108	[Rn] $5f^{14} 6d^6 7s^2$
Meitnerium 6	Mt†	109	[Rn] $5f^{14} 6d^7 7s^2$
Ununnilium	Uun*	110	[Rn] $5f^{14} 6d^8 7s^2$
(Darmstadtium)	(Ds)†		
Unununium	Uuu*	111	[Rn] $5f^{14} 6d^{10} 7s^1$
(Rontgenium)	(Rg)†		
Ununbium	Uub <sup>*</sup>	112	[Rn] $5f^{14} 6d^{10} 7s^2$

<sup>\*</sup>IUPAC names

The elements from atomic numbers 106 to 112 have recently been reported but these heavy elements are very unstable.

It is evident from the above electronic configurations that in transition elements ns-orbital is filled before (n-1)d-orbitals. Fig. 14.1 tells that near about atomic number 20, 4s-subshell has somewhat lower energy than 3d-subshell. Due to this, in potassium (Z=19) and calcium (Z=20), 4s-subshell is filled

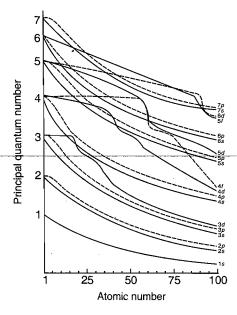


Fig. 14.1 The relative energies of the atomic orbitals as a function of atomic number

before 3*d*-subshell. Therefore, the electronic configurations of potassium and calcium are:

Potassium	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Calcium	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Beyond calcium, the energy of 3d-subshell is less than the energy of 4s and 4p-orbitals. Thus, 3d-orbitals are filled from scandium (Z=21) to zinc (Z=30). The filling of the 3d-orbitals proceeds one at a time. The d-orbitals are first occupied singly and then pairing starts. However, in two cases, chromium (Z=24) and copper (Z=29), one electron is present on 4s-orbital.

The unusual filling patterns in chromium and copper lead us to conclude that half filled and fully filled subshells are unexpectedly stable.

In the first series, 3*d*-electrons become more effective in shielding 4*s*-electrons from the nucleus, *i.e.*, 3*d*-electrons suffer more attraction than 4*s*-electrons from nucleus. This is apparent from the fact that when atoms of the elements from atomic

<sup>†</sup>American names

number 21 to 30 change into cations, the 4s-electrons are lost first before 3d-electrons, although 4s-subshell was filled earlier.

Mn	25	$(3d^54s^2)$	Mn <sup>2+</sup>	$3d^{5}$
Fe	26	$(3d^64s^2)$	Fe <sup>2+</sup>	$3d^6$
Ni	28	$(3d^84s^2)$	Ni <sup>2+</sup>	$3d^{8}$

The same thing is repeated in second transition series, *i.e.*, in the 5th period, the 5s-subshell is filled before 4d-subshell. In rubidium (Z = 37) and strontium (Z = 38), 5s-subshell is filled. 4d-subshell is gradually filled from yttrium (Z = 39) to cadmium (Z = 48). In 6th period, 6s-subshell is filled first before any electron is accommodated on 5d or 4f-orbitals. In lanthanum (Z = 57), the energies of 4f, 5d and 6s are very close to one another and after filling 6s-orbital in caesium (Z = 55) and barium (Z = 56), the next electron in lanthanum is accommodated on 5d-orbitals. In the subsequent elements from cerium (Z = 58) to lutetium (Z = 71) 4f-orbitals are gradually filled. From hafnium (Z = 72), the 5d-orbitals are filled. This process is completed in mercury.

Hf 72 
$$4f^{14}5d^26s^2$$
  
Hg 80  $4f^{14}5d^{10}6s^2$ 

Similar pattern in fourth transition series is observed.

The fourteen elements following lanthanum (Z = 57) from cerium (58) to lutetium (Z = 71) constitute the **first inner transition series.** These are also called **lanthanides.** In these elements 4f-orbitals are being filled successively. Similarly, the fourteen elements following actinium (Z = 89) from thorium (Z = 90) to lawrencium (Z = 103) constitute the second inner transition series. These are also called **actinides.** In these elements 5f-orbitals are successively filled.

#### ■ Conclusions

(i) An inner core of electrons with noble gas configuration is present.

Series	Inner core with noble gas
3 <i>d</i>	[Ar]
4 <i>d</i>	[Kr]
5d	[Xe]
6 <i>d</i>	[Rn]

- (ii) (n-1)d orbitals are filled up gradually with electrons, *i.e.*, configuration varies from  $(n-1)d^1$  to  $(n-1)d^{10}$ . Each series accommodates ten elements each.
- (iii) Most of the elements possess two electrons in the outermost orbital, *i.e.*,  $ns^2$ . However, some of the elements such as Cr, Cu, Nb, Mo, Tc, Ru, Rh, Ag, Pt, Au and Uuu have one electron in the outermost orbital, *i.e.*,  $ns^1$  while one element palladium has no electron on ns orbital.

# 14.3 GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

The members belonging to a given transition series do not differ so much from one another as those of representative elements of the same period. It is due to the fact that in a transition series, there is no change in the number of electrons of outermost shell and only change occurs in the (n-1)d electrons from member to member in a period. These elements show horizontal and vertical relationships or they show similarities in a period as well as in group. The general trends of some of the important properties are discussed here first in the respective periods and then in groups.

#### 1. Metallic Character

All the transition elements are metals. They exhibit most of the properties of metals. They possess metallic lustre, high density, high melting and boiling points, malleability, ductility, high tensile strength, hardness, brittleness, etc. They are good conductors of heat and electricity. They exhibit all the three types of structures: face centred cubic (fcc), hexagonal closed packed (hcp) and body centred cubic (bcc). These properties reveal that both metallic and covalent bonding are present in the atoms of transition elements.

The metallic bonding is due to possession of one or two electrons in the outermost energy shell like alkali and alkaline earth metals and relatively low ionisation energies. Copper, silver and gold are outstanding in their thermal and electrical conductivities. The properties of hardness and brittleness are associated with covalent bonding. The presence of unpaired and unfilled d-orbitals favours covalent bonding. Greater the number of unpaired d electrons, greater the number of covalent bonds and therefore, greater is the strength of these bonds. Cr, Mo and W are very hard metals as they have maximum number of unpaired d-orbitals while Zn, Cd and Hg are softer in nature as they do not have any unpaired d-orbitals.

#### 2. Atomic Radii

The atomic radii for transition metals are smaller than their corresponding s-block elements.

	s-block elements		Transitio	n metals
4th period	K	Ca	Sc	Cu
At. radius (pm)	203	174	144	117

The atomic radii\* of the elements of a given series decrease with increase in atomic number but this decrease becomes small after midway. In the first transition series, the atomic radius gradually decreases from scandium to chromium but from chromium to copper, it is nearly the same. Similar behaviour has been observed in the second and third transition series.

3d-series	At. radii (pm)	4d-series	At. radii (pm)	5d-series	At. radii (pm)
Sc	144	Y	162	La	168
Ti	132	Zr	145	Hf	144
V	122	Nb	134	Ta	134
Cr	117	Mo	130	w	130
Mn	117	Tc	*************	Re	128
Fe	117	Ru	125	Os	126
Co	116	Rh	125	Ir	1 <b>26</b>
Ni	115	Pd	128	Pt	129
Cu	117	Ag	134	Au	134
Zn	125	Cd	141	Hg	144

<sup>\*</sup> Covalent radii

The decrease in atomic radii in each series, in the beginning, is due to an increase in nuclear charge from member to member which tends to pull the ns electrons inward, i.e., it tends to reduce the size. At the same time, the addition of extra electrons to (n-1)d-orbitals also provides the screening effect. As the number of d electrons increases, the screening effect increases. Thus, there are operating two effects namely screening effect and nuclear charge effect which oppose each other. In the midway onwards of the series both these effects become nearly equal and thus, there is no change in atomic radii inspite of the fact that atomic number increases gradually.

The values of atomic radii at the end of each series are bit higher. This is due to electron-electron repulsions among (n-1)d electrons. These repulsions become predominant at the end of each series and thus size increases. It is evident from the atomic radii values of coinage and zinc metals.

In a vertical row, the atomic radii is expected to increase from top to bottom. Therefore, the atomic radii of transition metals of second series have larger values than those of the first transition series. However, the transition metals of third series except the first member, lanthanum, have nearly the same radii as metals of second transition series above them. This is due to **Lanthanide contraction**. Due to inclusion of fourteen lanthanides between lanthanum and hafnium, [there is continuous decrease in size from Ce(58) to Lu(71)] hafnium size becomes nearly equal to the size of zirconium.

#### 2 3. Ionic Radii

The ionic radii follow the same trend as the atomic radii. For the same oxidation state, the ionic radii generally decreases as the atomic number increases in a particular transition series.

The ionic radii decreases with increase of charge on the ion.

$$Fe^{3+}(0.64) < Fe^{2+}(0.76)$$
  
 $Ni^{3+}(0.62) < Ni^{2+}(0.72)$   
 $Mn^{3+}(0.66) < Mn^{2+}(0.80)$ 

The ionic radii of the transition metals are smaller than those of representative elements belonging to same period.

#### 4. Atomic Volumes and Densities

The atomic volumes of the transition elements are low as compared with elements in neighbouring groups I and II. This is because the nuclear charge is poorly screened and so attracts all the electrons more strongly.

Element Sc Ti V Cr Mn Fe Co Ni Cu Zn At. volume (mL) 
$$15.0 \ 10.6 \ 8.3 \ 7.23 \ 7.39 \ 7.10 \ 6.70 \ 6.60 \ 7.10 \ 9.20$$
 Density (g mL<sup>-1</sup>)  $3.0 \ 4.5 \ 6.1 \ 7.20 \ 7.40 \ 7.86 \ 8.90 \ 8.90 \ 8.96 \ 7.14$ 

Consequently, the densities of transition metals are high. The densities of second row are high and third row values are still higher. The two elements osmium and iridium have highest densities  $22.59~g~mL^{-1}$  and  $22.61~g~mL^{-1}$  respectively. Practically all the transition elements except scandium, yttrium and titanium possess density higher than  $5~g~mL^{-1}$ .

#### 5. Melting and Boiling Points

The transition metals have very high melting and boiling points. In each series, the melting points of these metals rise to a maximum value and then decrease with increase in atomic number. However, manganese and technetium have abnormally low melting points. The melting points of most of the transition elements except Zn, Cd and Hg are above 900°C. **Tungsten** has the highest melting point (3410°C) amongst transition elements.

The high melting and boiling points of transition metals are attributed to the stronger forces that bind their atoms together. The presence of one or more unpaired d electrons contributes to higher interatomic forces on account of covalent bonding and therefore, to high melting points. [However, this concept does not explain why manganese having five unpaired d electrons possesses lower melting point than that of vanadium or cobalt which have only three unpaired d electrons. The complex structure is responsible for this abnormal behaviour.]

When no unpaired electrons are present, the melting points are low as in the case of Zn, Cd and Hg.

```
3d-Series Sc Ti V Cr Mn Fe Co Ni Cu Zn M.pt. (°C) 1539 1668 1900 1875 1245 1536 1495 1453 1083 419.5 B.pt. (°C) 2730 3260 3450 2665 2150 3000 2900 2730 2595 906
```

#### 6. Ionisation Energies

The ionisation energy values of majority of d-block elements lie in between those of s- and p-block elements. The d-block elements are less electropositive than s-block elements and more electropositive than p-block elements. The transition elements do not form ionic compounds so readily as s-block elements do. Unlike s-block metals, transition elements form covalent compounds as well. Generally, lower valencies are ionic and higher valencies are covalent in nature. The first ionisation potential values are tabulated below in kJ  $\operatorname{mol}^{-1}$ .

Sc	Ti	V	Сг	Mn	Fe	Co	Ni	Cu	Zn
631	656	650	652	717	762	758	737	745	906
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
616	674	664	685	703	711	720	804	731	876
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
541	760	760	770	759	840	900	870	889	1007

Ionisation potential values increase in a period from left to right. The increase, however, is not regular. For example, in the case of first transition series, the ionisation potential values of Sc, Ti, V and Cr are fairly close to one another. Similarly, values of Fe, Co, Ni and Cu are almost similar.

The increase in the ionisation potential values in a given transition series is explained on the basis of increasing nuclear

charge and screening effect of (n-1)d electrons on ns electrons. With the increase of electrons in (n-1)d-subshell, the outer ns electrons are shielded more and more. Thus, the effect of increasing nuclear charge is somewhat neutralised by the additional screening effect and consequently, ionisation potential increases but quite slowly among a period of d-block elements. The value of zinc is appreciably higher due to additional stability associated with completely filled 3d-level in zinc. Slight variations that occur in ionisation potential values are mainly due to the slight changes in atomic radii.

Second and third ionisation energies, in general, also increase in a series. However, exceptions are observed.

3d series	Ind ionisation energy (kJ mol <sup>-1</sup> )	IIIrd ionisation energy (kJ mol <sup>-1</sup> )
Sc	1245	2451
Ti	1320	2721
$\mathbf{v}$	1376	2874
Cr	1635	2995
Mn	1513	3258
Fe	1564	2964 -
Co	1648	3238
Ni	1757	3401
, Cu,	1962	3561
Zn	1736	3839

Third ionisation energy of manganese is very high. This is because the third electron is to be removed from a stable configuration,  $(Mn^{2+}, 3d^5)$ , *i.e.*, half-filled 3d-subshell.

The second ionisation potential values of Cu and Cr are sufficiently higher than those of neighbouring elements. This is because of the electronic configuration of  $Cu^+$  which is  $3d^{10}$  (completely filled) and of  $Cr^+$  which is  $3d^5$  (half-filled), *i.e.*, for the second ionisation potential, the electron is to be removed from very stable configurations.

In vertical columns, *i.e.*, groups, the ionisation potential decreases from first member to second member in most of the cases as expected, however, the third member has higher value than second member. This is due to lanthanide contraction, *i.e.*, the atomic radii of the elements of the same group of the second and third transition series are nearly the same but atomic numbers differ by 32. Thus, the outer electrons are held very firmly and the ionisation potential values are very high. On account of this, the members of 5d are inert under ordinary conditions, *i.e.*, Pt, Au, Hg, etc., are noble metals.

#### 7. Standard Reduction Potentials

In solution, the stability of the compounds depends upon electrode potentials. Electrode potential value depends upon enthalpy of sublimation of the metal, the ionisation enthalpy and hydration enthalpy, *i.e.*,

$$M(s) \longrightarrow M^{+}(aq) + e \Delta H_{T}$$
 (Total energy change)

This process involves three steps:

First step

 $M(s) \longrightarrow M(g)$   $\Delta H_{\text{sub}}$  (Energy of sublimation) Second step

 $M(g) \longrightarrow M^{+}(g) + e$  I.E. (Ionisation energy) Third step

 $M^+(g) + aq \longrightarrow M^+(aq) \quad \Delta H_{\text{hyd}}$  (Hydration energy) Thus,  $\Delta H_T = \Delta H_{\text{sub}} + \text{I.E.} + \Delta H_{\text{hyd}}$ 

 $\Delta H_T$  is the total energy change when solid metal, M is brought in the aqueous medium in the form of monovalent ion,  $M^+(aq)$ .

The smaller the value of total energy change for a particular oxidation state in aqueous solution, greater will be the stability of that oxidation state. The electrode potentials are the measure of total energy change. Hence, quantitatively, the stability of the transition metal ions in different oxidation states in solution can be determined on the basis of the electrode potential data. The lower the electrode potential, i.e., more negative the standard reduction potential of the electrode, more stable is the oxidation state of the transition metal in the aqueous medium. The standard reduction potential values,  $E^{\circ}(M^{2+}/M)$  and  $(M^{3+}/M^{2+})$  of the members of first transition series are given below:

Element Ti V Cr Mn Fe Co Ni Cu Zn  $E^{\circ} (M^{2+}/M)V$  -1.63 -1.18 -0.91 -1.18 -0.44 -0.28 -0.25 +0.34 -0.76  $E^{\circ} (M^{3+}/M^{2+})V$  0.37 0.26 -0.41 +1.57 +0.77 +1.97 -- --

# ■ Trends in M<sup>2+</sup>/M Standard Electrode Potentials

- (i) It is evident that there is no regular trend in the  $E^{\circ}(M^{2+}/M)$  values. This is due to irregular variation of ionisation energies and sublimation energies of the atoms of the members of the transition series.
- (ii) Except copper, all other elements have negative reduction potential values, *i.e.*, these elements except copper should have the capacity to liberate hydrogen from dilute acids.

$$M + 2H^+$$
 (from acid)  $\longrightarrow M^{2+} + H_2 \uparrow$ 

In actual practice, the rate of liberation of hydrogen is very slow. Some of the metals, in fact, get protected by the formation of a thin film of an inert oxide on the surface. Chromium, for example, in spite of its high negative reduction potential value is an unreactive metal as it does not liberate hydrogen due to a thin coating of  $\text{Cr}_2\text{O}_3$  on its surface.

Copper having positive  $E^{\circ}$  value, does not liberate hydrogen from acids. It reacts only with oxidising acids such as HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub>.

THERM	OCHEMIC	CAL	DATA	(kJ	$mol^{-1}$ )	<b>FOR</b>
FIRST	SERIES	OF	<b>TRANS</b>	ITIO	N MET	ALS

Element (M)	ΔH <sub>sub</sub> (M)	LE. <sub>(i)</sub>	LE. <sub>(ii)</sub>	$\Delta H_{\text{hyd}}$ $(M^{2+})$
Ti	469	661	1310	1866
V	515	648	1370	-1895
Cr	398	653	1590	-1925
Mn	279	716	1510	-1862
Fe	418	762	1560	-1998
Co	427	757	1640	-2079
Ni	431	736	1750	-2121
Cu	339	745	1960	-2121
Zn	130	908	1730	-2059

- (iii) Less negative of  $E^{\circ}$  values along the series is due to increase in the first and second ionisation energies.
- (iv) The values of  $E^{\circ}$  for Mn, Zn and Ni are more negative than expected. This is due to extra stability of half-filled d-subshell ( $d^{5}$ ) in (Mn<sup>2+</sup>) and completely filled ( $d^{10}$ ) in Zn<sup>2+</sup>. The high value in Ni can be attributed due to high hydration energy.
- (v) In spite of the fact that all the metals except copper have negative  $E^{\circ}$  values, but are not good reducing agents in comparison to s-block elements. This is on account of high enthalpy of sublimation, high enthalpy of ionisation and poor enthalpy of hydration.

# ■ Trends in (M³+/M²+) Standard Electrode Potentials

- (i)  $E^{\circ}$  value for  $Sc^{3+}/Sc^{2+}$  is very low. Hence,  $Sc^{3+}$  is stable. This is due to its noble gas configuration.
- (ii)  $E^{0}$  value for  $Mn^{3+}/Mn^{2+}$  is high. This reflects that  $Mn^{2+}$  state is stable due to  $d^{5}$  configuration.
- (iii)  $E^{\circ}$  values for the redox couple  $M^{3+}/M^{2+}$  indicate that  $Mn^{3+}$  and  $Co^{3+}$  ions are strong oxidising agents.

#### 8. Oxidation States

The transition elements with the exception of a few show a large number of oxidation states. The various oxidation states are related to the electronic configuration of their atoms. The oxidation states of the members of first transition series are tabulated below. The oxidation states within brackets are not stable. The highest oxidation states are found in compounds with fluorine and oxygen because fluorine and oxygen are most electronegative in nature.

The variable oxidation states of a transition metal is due to the involvement of (n-1)d and outer ns electrons in bonding as the energies of ns and (n-1)d subshells are nearly equal. The lower oxidation state is generally shown by when ns-electrons participate in bonding and higher oxidation states are exhibited when ns and (n-1)d-electrons take part in bonding.

Element		Outer electronic configuration	Oxidation states
Sc	$3d^1,4s^2$	$\uparrow$ $3d$ $4s$	(+2), +3
Ti	$3d^2,4s^2$	$ \begin{array}{c cccc}  & & & & & & & & \\  & \uparrow & \uparrow & & & & & & \\  & \uparrow & \downarrow & & & & & \\  & \uparrow & \downarrow & & & & & \\ \end{array} $	(+2), +3, +4
v	$3d^3$ , $4s^2$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	+2, +3, +4, +5
Cr	$3d^5, 4s^1$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(+1), +2, +3, (+4), (+5), +6
Mn	$3d^5,4s^2$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	+2, +3, +4, (+5), +6, +7
Fe	$3d^6,4s^2$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	+2, +3, (+4), (+5), (+6)
Co	$3d^{7},4s^{2}$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	+2, +3, (+4)
Ni	$3d^8,4s^2$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	+2, +3, +4
Cu	$3d^{10},4s^1$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	+1, +2
Zn	$3d^{10},4s^2$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	+2

From the survey of the oxidation states of transition elements, the following conclusions are drawn:

- (i) Generally, within the transition series, the highest oxidation state increases with increase of atomic number, reaching to a maximum in the middle and then starts decreasing. For example, in the first transition series manganese shows the maximum oxidation state of +7. The highest oxidation state shown by any transition metal is +8. Ruthenium in second transition series and osmium in the third transition series show +8 oxidation state.
- (ii) In general, the minimum oxidation state shown by a transition metal is equal to the number of ns-electrons. Except scandium, (which has +3 oxidation state) for the elements of first transition series +2 oxidation state is the most common. This state arises due to loss of 4s-electrons. However, for chromium and copper, the lowest oxidation state is +1. This is due to their electronic configurations, Cr(3d<sup>5</sup>4s<sup>1</sup>) and Cu(3d<sup>10</sup>4s<sup>1</sup>). Thus, it is evident that after scandium d-orbitals are more stable than 4s-orbital, i.e., the energy associated with 3d-subshell is less than that of 4s-subshell.
- i.e., upto manganese (3d-subshell is no more than half-filled), the maximum oxidation state is equal to the sum of the 4s and 3d-electrons. For example, maximum oxidation state for titanium is  $+4 (3d^24s^2)$ , for vanadium  $+5(3d^34s^2)$ , for chromium  $+6(3d^54s^1)$  and for manganese, it is  $+7 (3d^54s^2)$ . For the remaining five elements the maximum oxidation state is not related to their electronic configurations. The common oxidation states for the elements from Fe to Ni are +2 or +3. The oxidation state higher than +3 is rarely shown.

(iii) In the first five elements of the first transition series,

- (iv) Some of the transition metals form compounds in zero oxidation state. The common examples are Ni(CO)<sub>4</sub> and Fe(CO)<sub>5</sub> in which nickel and iron are in zerovalent state.
- (v) In +2 and +3 oxidation states, the bonds formed are mostly ionic. On the other hand, in higher oxidation states, the bonds formed are essentially covalent. Higher states are usually attained with elements of high electronegativity such as fluorine and oxygen. For example, in the ions such as CrO<sub>4</sub><sup>2-</sup>, MnO<sub>4</sub><sup>-</sup>, the bonds formed are covalent.
- (vi) The relative stability of various oxidation states of a given element can be explained on the basis of stability of  $d^0$ ,  $d^5$  and  $d^{10}$  configurations. For example,

 $Ti^{4+}$   $(3d^04s^0)$  is more stable than  $Ti^{3+}$   $(3d^14s^0)$ ;  $Mn^{2+}(3d^54s^0)$  is more stable than  $Mn^{3+}$   $(3d^44s^0)$ ;  $Fe^{3+}$   $(3d^54s^0)$  is more stable than  $Fe^{2+}(3d^64s^0)$ , etc. The relative stabilities of various oxidation states of a given element can also be explained on the basis of standard electrode potential data. For example, in case of copper we have

$$Cu^+(aq) + e^- \longrightarrow Cu(s); \quad E^o = 0.52 \text{ V}$$
  
 $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s); \quad E^o_{red} = 0.34 \text{ V}$ 

Thus, Cu<sup>+</sup> is reduced easily and hence is less stable than Cu<sup>2+</sup>.

- (vii) In a group of d-block elements, the higher oxidation states are more stable for heavier elements. For example, in group 6, Mo(vi) and W(vi) are more stable than Cr(vi). For example, dichromate having Cr(vi) is a strong oxidising agent in acidic medium while MoO<sub>3</sub> and WO<sub>3</sub> are stable oxides.
- (viii) In transition elements the successive oxidation states differ by unity.

A substance appears coloured because it absorbs light atspecific wavelengths in the visible part of the electromagnetic spectrum (4000 to 7000Å) and transmits or reflects the rest of the wavelengths. Each wavelength of visible light represents a different colour. White light is a combination of all colours. The table given shows the relationship of wavelength absorbed to the observed colour.

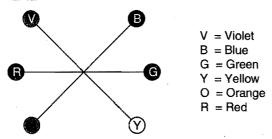
Wavelength absorbed (Å)	Colour observed
4000 (Violet)	Greenish yellow
4500 (Blue)	Yellow
· 4900 (Blue-green)	Red
5700 (Yellowish green)	Violet
5800 (Yellow)	Dark blue
6000 (Orange)	Blue
6500 (Red)	Blue-green

Most of the compounds of transition metals are coloured in the solid or in solution states. The colour of transition metal ions arises from the excitation of electrons from the d-orbitals of lower energy to the d-orbitals of higher energy. The energy required for d-d electron excitations is available in the visible range. It is for this reason that transition metal ions have the property to absorb certain radiations from the visible region and exhibit the complementary colour. The colours and outer electronic configurations of important ions of the elements of first transition series are tabulated ahead:

COLOURS AND MAGNETIC MOMENTS OF IONS OF	
THE FIRST TRANSITION SERIES	

Ion	Outer configuration	Number of unpaired electrons	Colour of the	Magnetic moment (B.M.)
Sc <sup>3+</sup> Ti <sup>4+</sup> Ti <sup>3+</sup> V <sup>3+</sup> Cr <sup>3+</sup> Mn <sup>3+</sup>	$3d^0$ $3d^0$	0	Colourless	0
Ti <sup>4+</sup>	$3d^0$	0	Colourless	0
Ti <sup>3+</sup>	$3d^1$	1	Purple	1.75
$V^{3+}$	$3d^{2}$ $3d^{3}$ $3d^{4}$ $3d^{5}$ $3d^{6}$	2	Green	2.76
Cr <sup>3+</sup>	$3d^3$	3	Violet .	3.86
Mn <sup>3+</sup>	$3d^4$	4	Violet	5.0
Mn <sup>2+</sup> Fe <sup>2+</sup> Fe <sup>3+</sup> Co <sup>2+</sup>	$3d^5$	5	Light pink	5.96
Fe <sup>2+</sup>	$3d^6$	4	Green	5.10
Fe <sup>3+</sup>	$3d^5$	5	Yellow	5.96
Co <sup>2+</sup>	$3d^7$	3	Pink	4.4 - 5.2
Ni <sup>2+</sup>	$3d^8$	2	Green	2.9 - 3.4
Cu <sup>2+</sup>	$3d^9$ $3d^{10}$	1	Blue	1.8 – 2.2
Cu <sup>+</sup>	$3d^{10}$	0	Colourless	0
$Zn^{2+}$	$3d^{10}$	. 0	Colourless	0

Complementary colours can be identified using Munshel colour wheel.



Opposite colours are complementary.

The transition metal ions which have completely filled d-orbitals  $(3d^{10}, 4d^{10} \text{ or } 5d^{10})$  such as  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Hg^{2+}$ ,  $Cu^{+}$ ,  $Ag^{+}$  and  $Au^{+}$  ions are colourless as the excitation of electron or electrons is not possible within d-orbitals. The transition metal ions which have completely empty d-orbitals such as  $Sc^{3+}$ ,  $Ti^{4+}$ , etc., are also colourless.

[Note: In the oxysalts of transition elements like KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, there are no unpaired electrons at the central atom but they are deep in colour. The colour of these compounds is due to charge transfer spectrum.

Observe the colour of following compounds of silver

	AgCl	AgBr	AgI	Ag <sub>2</sub> S
Colour	White	Pale Yellow	Yellow	Black
% Ionic character $A\sigma^{+} = 4d^{10}5s^{0}$	80%	24%	15%	4%

There is no unpaired electron with Ag<sup>+</sup>. Thus, colour of these compounds can be explained on the basis of percentage ionic character.

If the ionic character of these ionic compounds is less than 20% then the compound will be coloured.]

1 B.M.=
$$\frac{eh}{4\pi mc}$$
 B.M. = Bohr-magneton

#### 10. Magnetic Properties

Majority of substances show magnetic nature. These are either **paramagnetic** or **diamagnetic**. A paramagnetic substance is one which is weakly attracted into a magnetic field and a diamagnetic substance is one which is repelled by a magnetic field. The paramagnetic behaviour arises due to the presence of one or more singly occupied atomic orbitals, while diamagnetic behaviour is due to presence of paired electrons in the atomic orbitals.

Most of the compounds of transition elements are paramagnetic in nature as unpaired electrons in d-subshell are present. The magnetic character is expressed in terms of magnetic moment. The magnetic moments arise only from the spin of electrons. The effective total magnetic moment,  $\mu_{eff}$ , is given by the expression.\*

$$\mu_{\text{eff}} = \sqrt{n(n+2)}$$
 B.M.

where n is the number of unpaired electrons. Larger the number of unpaired electrons in a substance, the greater is its magnetic moment in Bohr-magneton and larger shall be its paramagnetism. The magnetic moments of some important ions of the elements of first transition series are given in the table.

It is evident from the values that the magnetic moments or paramagnetic behaviour increases as the number of unpaired electrons increases from 1 to 5. After  $d^5$  configuration, there is decrease in magnetic moment as the number of unpaired electrons decreases.

In the case of iron, cobalt and nickel the unpaired electron spins are much more pronounced. As a result, these elements are much more paramagnetic than the rest of the elements.

These elements are termed ferromagnetic and can be magnetised.

#### 11. Tendency to form Complexes

d-block elements have a marked ability to form complex compounds. This ability is on account of following three reasons:

(i) Small size (ii) high nuclear charge (iii) a number of vacant orbitals of equivalent energy where, the electrons donated by ligands can be accommodated. Ligands are species with lone pair of electrons which they can readily donate. These species can be neutral molecules such as NH<sub>3</sub>, H<sub>2</sub>O, NO, CO, etc., or ions such as F<sup>-</sup>, Cl<sup>-</sup>, CN<sup>-</sup>, etc.

The number of attachment with ligands are usually either four or six, *i.e.*, the coordination number of metal ion is usually four or six. The compounds containing complex ions are termed as coordination compounds. Na<sub>3</sub>[Fe(CN)<sub>6</sub>], [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>, [Cr(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> and Ni(CO)<sub>4</sub> are some of the examples of

<sup>\*</sup> This expression is applicable mainly to 3d elements.

 $e = \text{Charge of electron}; \ h = \text{Planck constant}; \ m = \text{Mass of electron}; \ c = \text{Velocity of light}$ 

coordination compounds. Coordination compounds are discussed in detail in chapter 15.

#### 12. Formation of Interstitial Compounds

Small non-metallic atoms such as H, B, C, N, etc., are able to occupy interstitial spaces of the lattices of the d-block elements to form combinations which are termed interstitial compounds. These are non-stoichiometric in nature and do not follow the common rules of valency. The bonds present are neither typically ionic nor covalent. The formulae do not correspond to any normal oxidation state of the metal.

Some of the characteristics of interstitial compounds are:

- (i) The interstitial compounds have similar chemical properties as the parent metals but differ appreciably in their physical properties such as density, conductivity, hardness, etc.
- (ii) As a result of filling up of the interstitial spaces, the metals become rigid and hard. Steel is quite hard as it is interstitial compound of Fe and C. Some of the borides are as hard as diamond.
- (iii) Interstitial compounds possess high melting points which are higher than those of pure metals.

#### 3 13. Catalytic Properties

Many of the *d*-block elements and their compounds act as catalysts in various reactions. Some common examples are:

- (i) Pt—used as a catalyst in the manufacture of H<sub>2</sub>SO<sub>4</sub>.
- (ii) Fe—used as a catalyst in the manufacture of NH<sub>3</sub> by Haber process. A small amount of molybdenum is added as a promoter.
- (iii) Ni—used as a catalyst in the hydrogenation of oils.
- (iv) V<sub>2</sub>O<sub>5</sub>—used as a catalyst for the oxidation of SO<sub>2</sub> into SO<sub>3</sub> for the manufacture of H<sub>2</sub>SO<sub>4</sub> in the contact process.
- (v) MnO<sub>2</sub>—used as a catalyst in the decomposition of KClO<sub>3</sub> for preparation of oxygen.
- (vi) Cobalt salts catalyse the decomposition of bleaching powder.

Catalytic property is probably due to the utilisation of (n-1)d-orbitals or formation of interstitial compounds.

#### 14. Alloy Formation

Transition metals form a large number of alloys. Since d-block elements are quite similar in atomic size, the atoms of one metal can substitute the atoms of other metal in its crystal lattice. Thus, on cooling a mixture solution of two or more transition metals, smooth solid alloys are formed.

Alloys containing mercury as one of the constituent elements are called **amalgams**. The purpose of making alloys is to develop some useful properties which are absent in the constituent elements.

#### **15. Some Important Compounds**

The transition metals combine with a number of non-metals such as oxygen, nitrogen, carbon, halogens, sulphur and phosphorus, etc., to form useful binary compounds. General trends in oxides, halides and sulphides are discussed.

(a) Oxides: The elements of first transition series form a number of oxides having general formulae MO,  $M_2O_3$ ,  $M_3O_4$ ,  $MO_2$ ,  $M_2O_5$ ,  $MO_3$ . The oxides are generally formed when the metals are strongly heated at high temperature in the atmosphere of oxygen. These oxides exhibit acidic, basic and amphoteric behaviour. The important and common oxides of the elements of first transition series are listed in the following table:

# OXIDES OF THE METALS OF FIRST TRANSITION SERIES

Sc		$Sc_2O_3(b)$			
Ti	TiO(b)	$Ti_2O_3(b)$	$TiO_2(c)$	,	
V	VO(b)	$V_2O_3(b)$	VO <sub>2</sub> (c)	$V_2O_5(a)$	con a menimbanden I dimerciden an sambilitation and discover anno belle "
Cr	CrO(b)	Cr <sub>2</sub> O <sub>3</sub> (c)	CrO <sub>2</sub> (c)		CrO <sub>3</sub> (a)
Mn	MnO(b)	$Mn_2O_3(b)$	MnO <sub>2</sub> (c)	Mn <sub>3</sub> O <sub>4</sub> (c)	$[MnO_3(a)]Mn_2O_7(a)$
Fe	FeO(b)	$Fe_2O_3(b)$		Fe <sub>3</sub> O <sub>4</sub> (b)	
Co	CoO(b)	$[\mathbf{Co_2O_3^h(b)}]$	[[CoO <sup>h</sup> 2]	· · · ·	
Ni	NiO(b)	$[Ni_2O_3^h(b)]$	$NiO_2^h$	Mixed	
Cu	CuO(b)		•		
Zn	ZnO(b)				

where a = acidic; b = basic; c = amphoteric; h = hydrated

[Note: Stable oxides have been indicated by bold letters. Unstable are in parentheses.]

- (i) The oxides in lower oxidation states are basic in nature.
- (ii) The oxides in intermediate oxidation states are amphoteric.
  - (iii) The oxides of higher oxidation states are acidic in nature. **Examples:**

#### Oxides of chromium:

#### Oxides of manganese:

It can also be said that if a metal forms a number of oxides, the acidic nature of the oxides increases as the percentage of oxygen increases.

(iv) The basic and amphoteric oxides generally dissolve in non-oxidising acids like HCl to form hexaaquo ions,  $[M(H_2O)_6]^{n+}$ .

- (v) Some of the oxides dissolve in acids or bases to form oxometallic salts such as chromates, dichromates, permanganates, etc.
- (b) Halides: Transition metals combine with halogens at high temperatures to form compounds called halides. On account of high activation energies of these reactions, high temperature is usually needed to start the reaction, but once the reaction starts, the heat of reaction is sufficient to maintain the continuity of the reaction (Reactions are exothermic in nature). The order of the reactivity of halogens is:

Metals in higher oxidation states only form fluorides as it is the most electronegative and reactive element. The following are some of the general characteristics of halides.

(i) Fluorides are mainly ionic in nature. The chlorides, bromides and iodides have ionic as well as covalent character. The covalent character increases as atomic mass of the halogen increases. For example, CuF<sub>2</sub> is ionic compound while CuCl<sub>2</sub> and CuBr<sub>2</sub> are covalent forming infinite chains. The coordination number of the copper in these compounds is six. The structure of CuCl<sub>2</sub> is given below:

(ii) Halides of metals in higher oxidation states are relatively unstable and undergo hydrolysis very easily.

$$TiCl_4 + 2H_2O \longrightarrow TiO_2 + 4HCl$$

The solutions of several halides are acidic in nature due to hydrolysis. These solutions can be stabilised by addition of acids in order to prevent hydrolysis.

$$FeCl_3 + 3H_2O \implies Fe(OH)_3 + 3HCl$$
  
 $CuCl_2 + 2H_2O \implies Cu(OH)_2 + 2HCl$ 

(c) Sulphides: Sulphides of transition metals can be formed either by direct combination of the metals with sulphur or by action of H<sub>2</sub>S or Na<sub>2</sub>S on the salts of these metals.

Fe + S 
$$\longrightarrow$$
 FeS  
CuSO<sub>4</sub> + H<sub>2</sub>S  $\longrightarrow$  CuS + H<sub>2</sub>SO<sub>4</sub>  
2AgNO<sub>3</sub> + Na<sub>2</sub>S  $\longrightarrow$  Ag<sub>2</sub>S + 2NaNO<sub>3</sub>

Sulphides of transition metals are coloured usually black and are insoluble in water.

## 14.4 CHEMISTRY OF CHROMIUM

Chromium belongs to group 6 (VI B) of the extended form of periodic table. The other members of the group are molybdenum (Mo) and tungsten (W). The most abundant element of this group is chromium. The most important ore of chromium is **chromite** or **chrome-iron stone**, FeO·Cr<sub>2</sub>O<sub>3</sub>.

The concentrated ore is mixed with excess of sodium carbonate and roasted in a reverberatory furnace in a free supply of air.  $Cr_2O_3$  present in the ore is converted into sodium chromate.

The roasted mass is extracted with water when Na<sub>2</sub>CrO<sub>4</sub> goes into solution leaving behind insoluble Fe<sub>2</sub>O<sub>3</sub> and unconverted ore. The solution is treated with calculated amount of sulphuric acid to convert sodium chromate into dichromate.

$$2Na_2CrO_4+H_2SO_4 \longrightarrow Na_2Cr_2O_7+Na_2SO_4+H_2O_7$$

The solution is concentrated when less soluble Na<sub>2</sub>SO<sub>4</sub> crystallises out. The solution is further concentrated when crystals of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> are obtained. Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is heated with carbon and the chromite thus formed is extracted with water when Cr<sub>2</sub>O<sub>3</sub> is precipitated.

$$Na_2Cr_2O_7 + 3C \longrightarrow Na_2Cr_2O_4 + 3CO$$
  
Sodium chromite

$$Na_2Cr_2O_4 + H_2O \longrightarrow 2NaOH + Cr_2O_3$$

Reduction of Cr<sub>2</sub>O<sub>3</sub> is done by Goldsmith alumino-thermic process.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$

The mixture is taken in the ratio of 3:1 in a refractory crucible and the mixture is ignited with burning magnesium ribbon. The metal obtained is about 92% pure. It is further purified electrolytically using mercury as cathode and chromic chloride solution as electrolyte. The amalgam is finally heated in vacuum to get 99.7% pure metal.

**Ferrochrome:** An alloy of Cr and Fe containing about 75% Cr is obtained when chromite ore is reduced with carbon in an electric furnace.

$$FeO \cdot Cr_2O_3 + 4C \longrightarrow Fe + 2Cr + 4CO$$
Alloy

Ferrochrome is extensively used for alloying with iron to make special steels.

#### Uses

- (i) Chromium is used in making alloys such as chrome steels, stainless steel (18% Cr) and nichrome (Ni 60%, Fe 25%, Cr 15%).
- (ii) It is extensively used for plating metals because it is very resistant to corrosion.
  - (iii) Its compounds find wide applications.

The outer electronic configuration of chromium is  $3d^54s^1$ . It exhibits a large number of oxidation states varying from O to +6. The stable and important oxidation states of Cr are +2, +3 and +6. Chromium (II) compounds are reducing agents as they are readily converted into chromium (III) compounds even by the oxygen of the air. +3 oxidation state is highly stable in acid solutions but it gets oxidised readily to +6 oxidation

state in alkali solutions. Chromium compounds in +6 oxidation states are strong oxidising agents.

#### 14.5 POTASSIUM DICHROMATE, K2Cr2O7

It is the most important compound of Cr (VI). It is manufactured from chromite ore. Chromite ore is first converted into sodium dichromate as described in section 14.4. The hot saturated solution of sodium dichromate is mixed with KCl. Sodium chloride precipitates out from the hot solution which is filtered off. On cooling the mother liquor, crystals of potassium dichromate separate out.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

#### Properties

It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C. On heating strongly, it decomposes liberating oxygen.

$$2K_2Cr_2O_7 \longrightarrow 2K_2CrO_4 + Cr_2O_3 + \frac{3}{2}O_2$$

On heating with alkalies, it is converted to chromate, *i.e.*, the colour changes from orange to yellow. On acidifying, yellow colour again changes to orange.

$$\begin{array}{c} K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O \\ Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O \\ \text{Orange} \qquad \qquad \text{Yellow} \\ 2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O \\ \text{Yellow} \qquad \qquad \text{Orange} \end{array}$$

In alkaline solution, chromate ions are present while in acidic solution, dichromate ions are present. Both the ions are in equilibrium at pH = 4.

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$$

Potassium dichromate reacts with hydrochloric acid and evolves chlorine.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

It acts as a powerful exidising agent in acidic medium (dilute  $H_2SO_4$ ).

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Cold concentrated solution of  $K_2Cr_2O_7$ , on treatment with concentrated  $H_2SO_4$  forms chromic anhydride (CrO<sub>3</sub>).

The oxidation state of Cr changes from +6 to +3.

The potential equation in terms of available oxygen can be given as:

$$\begin{array}{c} K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O] \\ \text{1 mole} \\ \end{array}$$

Thus, the equivalent mass of  $K_2Cr_2O_7$  in acidic medium is  $\frac{\text{Mol. mass}}{6}$ , i.e.,  $\frac{294}{6} = 49$ .

Some typical oxidation reactions are given below:

(i) Iodine is liberated from potassium iodide.

$$K_2Cr_2O_7+4H_2SO_4 \longrightarrow K_2SO_4+Cr_2(SO_4)_3+4H_2O+3[O]$$
  
 $[2KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + I_2 + H_2O] \times 3$ 

$$K_2Cr_2O_7+6KI+7H_2SO_4 \longrightarrow 4K_2SO_4+Cr_2(SO_4)_3+7H_2O+3I_2$$

The equation in terms of electron method may also be written as

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
  
 $6I^- \longrightarrow 3I_2 + 6e^-$   
 $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$ 

(ii) Ferrous salts are oxidised to ferric salts.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$
  
 $[2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 3$ 

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 7H_2O + K_2SO_4$$

or 
$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

(iii) Sulphites are oxidised to sulphates.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$
  
 $[Na_2SO_3 + [O] \longrightarrow Na_2SO_4] \times 3$ 

$$\begin{array}{c} K_2Cr_2O_7 + 3Na_2SO_3 + 4H_2SO_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + K_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 \longrightarrow 3Na_2SO_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 + \\ Cr_2(SO_4)_3 + 4H_2O_4 + \\ Cr_2(SO_4)_4 + Cr_2(SO_4)_5 + \\ Cr_2(SO_4)_5 + Cr_2(SO_4)_5$$

or 
$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$$

(iv) H<sub>2</sub>S is oxidised to sulphur.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$
  
or  $Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 3S$ 

(v) SO<sub>2</sub> is oxidised to H<sub>2</sub>SO<sub>4</sub>.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$
  
 $[SO_2 + [O] + H_2O \longrightarrow H_2SO_4] \times 3$ 

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$
  
or  $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$ 

When the solution is evaporated, chrome-alum is obtained. (vi) It oxidises ethyl alcohol to acetaldehyde and acetaldehyde to acetic acid.

$$\begin{array}{c} C_2H_5OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH \\ \text{Ethyl alcohol} & \text{Acetaldehyde} \end{array}$$

It also oxidises nitrites to nitrates, arsenites to arsenates, thiosulphate to sulphate and sulphur  $(S_2O_3^{2-} + O \longrightarrow SO_4^{2-} + S)$ , HBr to Br<sub>2</sub>, HI to I<sub>2</sub>, etc.

$$Cr_2O_7^{2-} + 8H^+ + 3NO_2^- \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$
  
 $Cr_2O_7^{2-} + 8H^+ + 3S_2O_3^{2-} \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 3S + 4H_2O$   
 $K_2Cr_2O_7 + 14HBr \longrightarrow 2KBr + 2CrBr_3 + 7H_2O + 3Br_2$   
 $K_2Cr_2O_7 + 14HI \longrightarrow 2KI + 2CrI_3 + 7H_2O + 3I_2$ 

(vii) Chromyl chloride test: This is a test of chloride. When a mixture of a metal chloride and potassium dichromate is heated with conc.  $H_2SO_4$ , orange-red vapours of chromyl chloride are evolved.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$$
  
 $[NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl] \times 4$   
 $[CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O] \times 2$ 

$$\begin{array}{c} K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl \longrightarrow 2KHSO_4 + 4NaHSO_4 \\ + 2CrO_2Cl_2 + 3H_2O \\ \hline \\ Chromyl \ chloride \end{array}$$

When chromyl chloride vapours are passed through NaOH solution, yellow coloured solution is obtained.

$$4NaOH + CrO_2Cl_2 \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$
  
Yellow soln.

The yellow coloured solution on acidification with acetic acid followed by addition of lead acetate gives thick yellow precipitate of lead chromate.

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4 + 2CH_3COONa$$
  
Lead chromate  
(yellow ppt.)

[Note: This test is not positive with the chlorides of Hg, Ag, Pb and Sn.]

(viii) Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution reacts with hydrogen peroxide to give a deep blue solution due to formation of CrO<sub>5</sub>. It is unstable and blue colour fades away gradually due to formation of chromic sulphate.

$$K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + H_2Cr_2O_7$$
 $(conc.)$ 
 $[H_2O_2 \longrightarrow H_2O + O] \times 4$ 
 $H_2Cr_2O_7 + 4[O] \longrightarrow 2CrO_5 + H_2O$ 

$$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow 2CrO_5 + K_2SO_4 + 5H_2O_4$$
 $4CrO_5 + 6H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 6H_2O + 7O_2$ 
 $CrO_4$  (perovide of abromium) is represented as

CrO<sub>5</sub> (peroxide of chromium) is represented as

#### ■ Some Miscellaneous Reactions

(a) Powdered  $K_2Cr_2O_7$  on treatment with warm concentrated HCl forms petigot's salt.

K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2HCl 
$$\longrightarrow$$
 2KCrO<sub>3</sub>Cl + H<sub>2</sub>O

Potassium
chlorochromate
(Petigot's salt)

(b) With  $K_2CO_3$ ,  $K_2Cr_2O_7$  forms potassium chromate.  $K_2Cr_2O_7 + K_2CO_3 \longrightarrow 2K_2CrO_4 + CO_2$  (c) Potassium dichromate on heating with carbon is reduced to potassium chromite which on treatment with water gives chromium sesquioxide.

$$K_2Cr_2O_7 + 3C \longrightarrow K_2Cr_2O_4 + 3CO$$
  
 $K_2Cr_2O_4 + H_2O \longrightarrow 2KOH + Cr_2O_3$ 

(d) When potassium dichromate and ammonium chloride mixture is heated, nitrogen is evolved.

$$K_2Cr_2O_7 + 2NH_4Cl \xrightarrow{Heat} 2KCl + Cr_2O_3 + N_2 + 4H_2O$$

(e) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, on fusion with K<sub>4</sub>Fe(CN)<sub>6</sub>, potassium cyanate is formed.

$$\frac{2K_2Cr_2O_7 + 2K_4Fe(CN)_6 \longrightarrow 6KCNO + 2Cr_2O_3 + 2K_2O}{+ K_2Fe[Fe(CN)_6]}$$

Structure of chromate and dichromate ions: The chromate ion has a tetrahedral structure. In dichromate, two tetrahedral sharing one oxygen atom at one corner are present.

#### Uses

Potassium dichromate is used (i) as a volumetric reagent in the estimation of reducing agents such as oxalic acid, ferrous ions, iodide ions, etc. It is used as a primary standard. (ii) for the preparation of several chromium compounds such as chrome alum, chrome yellow, chrome red, zinc yellow, etc. (iii) in dyeing, chrome tanning, calico printing, photography, etc. (iv) chromic acid as a cleansing agent for glassware. (v) in organic chemistry as an oxidising agent (vi) as laboratory reagent. (vii) Acidified solution of  $K_2Cr_2O_7$  provides a test to find out whether a person is drunken or not. A person is asked to breathe into a solution of  $K_2Cr_2O_7$  (acidified). If the colour of the solution turns green, it confirms that the person is in drunken state.

#### 14.6 CHEMISTRY OF MANGANESE

Manganese is a member of group 7 (VIIB). The other members of the group are technetium (Tc) and rhenium (Re). Of these elements, only manganese is important. It is twelfth most abundant element by mass in earth's crust. Technetium is not

found in nature and was the first man-made element. Rhenium is a very rare element. The important ores of manganese are:

- (i) Pyrolusite, MnO<sub>2</sub>
- (ii) Braunite, Mn<sub>2</sub>O<sub>3</sub> and
- (iii) Hausmannite, Mn<sub>3</sub>O<sub>4</sub>.

Manganese is obtained from its oxide ore generally pyrolusite or hausmannite by reduction with carbon or aluminium.

Since MnO<sub>2</sub> gives an explosive reaction with aluminium, it is first converted into manganomanganic oxide, Mn<sub>3</sub>O<sub>4</sub>, by heating to redness. This is then reduced with aluminium in fire-clay crucible embedded in sand.

$$3MnO_2 \longrightarrow Mn_3O_4 + O_2$$
  
 $3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$ 

Manganese is purified by distillation in vacuum.

The chief use of manganese is in steel production. 95% of the manganese ores mined are used in steel industry to produce alloys. The mixed oxides of iron and manganese are reduced by heating in a blast furnace along with carbon. Two important alloys are *ferromanganese* (80% Mn and 20% Fe) and spiegeleisen (20 - 30% Mn, 5% C and rest Fe).

The outer electronic configuration of manganese is  $3d^54s^2$ . It exhibits a large number of oxidation states varying from 0 to +7. The zero oxidation state is observed in carbonyls. The +2 state is the most stable and most common. Manganese exhibits +3, +4, +6 and +7 oxidation states. In +7 state the permanganates are strong oxidising agent. +4 and +7 states are also stable. Manganese forms a number of oxides. The basic nature decreases while acidic nature increases as the oxidation state increases.

Manganous Manganic Manganites Manganates Permangasalts salts nates

Manganese also forms a mixed oxide, Mn<sub>3</sub>O<sub>4</sub>, which is a combination of MnO and Mn<sub>2</sub>O<sub>3</sub>. It is known as manganomanganic oxide.

# 14.7 POTASSIUM PERMANGANATE, KMnO<sub>4</sub>

This is the most important and well known salt of permanganic acid. It is prepared from the pyrolusite ore. It is prepared by fusing pyrolusite ore either with KOH or K<sub>2</sub>CO<sub>3</sub> in presence of atmospheric oxygen or any other oxidising agent such as KNO<sub>3</sub>. The mass turns green with the formation of potassium manganate, K<sub>2</sub>MnO<sub>4</sub>.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$
  
 $2MnO_2 + 2K_2CO_3 + O_2 \longrightarrow 2K_2MnO_4 + 2CO_2$ 

The fused mass is extracted with water. The solution is now treated with a current of chlorine or ozone or carbon dioxide to convert manganate into permanganate.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$
$$3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$$

Now-a-days, the conversion is done electrolytically.

It is electrolysed between iron cathode and nickel anode. Dilute alkali solution is taken in the cathodic compartment and potassium manganate solution is taken in the anodic compartment. Both the compartments are separated by a diaphragm. On passing current, the oxygen evolved at anode oxidises manganate into permanganate.

At anode:

$$2K_{2}MnO_{4} + H_{2}O + O \longrightarrow 2KMnO_{4} + 2KOH$$

$$MnO_{4}^{2-} \longrightarrow MnO_{4}^{-} + e$$
Green Purple

At cathode:

$$2H^+ + 2e \longrightarrow H_2$$

The anodic solution is concentrated under controlled conditions. when crystals of potassium permanganate are obtained.

## Properties

It is purple coloured crystalline compound. It is fairly soluble in water. When heated alone or with an alkali, it decomposes evolving oxygen.

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$
  
 $4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$ 

On treatment with conc.  $H_2SO_4$ , it forms manganese heptoxide via permanganyl sulphate which decomposes explosively on heating.

$$\begin{array}{c} 2KMnO_4 + 3H_2SO_4 \longrightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O \\ (MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4 \\ Mn_2O_7 \longrightarrow 2MnO_2 + \frac{3}{2}O_2 \end{array}$$

Potassium permanganate is a powerful oxidising agent. A mixture of sulphur, charcoal and KMnO<sub>4</sub> forms an explosive powder. A mixture of oxalic acid and KMnO<sub>4</sub> catches fire spontaneous after a few seconds. The same thing happens when glycerine is poured over powdered KMnO<sub>4</sub>.

Potassium permanganate acts as an oxidising agent in alkaline, neutral or acidic solutions.

(a) In alkaline solution: KMnO<sub>4</sub> is first reduced to manganate and then to insoluble manganese dioxide. Colour changes first from purple to green and finally becomes colourless. However, brownish precipitate is formed.

$$\begin{array}{c} 2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + O \\ 2K_2MnO_4 + 2H_2O \longrightarrow 2MnO_2 + 4KOH + 2O \\ \hline 2KMnO_4 + H_2O \xrightarrow{Alkaline} 2MnO_2 + 2KOH + 3[O] \\ or 2MnO_4 + H_2O \longrightarrow 2MnO_2 + 2OH + 3[O] \end{array}$$

(b) In neutral solution:  $MnO_2$  is formed. Brownish ppt. is present.

$$2KMnO_4 + H_2O \longrightarrow 2MnO_2 + 2KOH + 3[O]$$
or 
$$2MnO_4^- + H_2O \longrightarrow 2MnO_2 + 2OH^- + 3[O]$$
or 
$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

(c) In acidic solution (in presence of dilute H<sub>2</sub>SO<sub>4</sub>): Manganous sulphate is formed. The solution becomes colourless.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
or 
$$2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5[O]$$
or 
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

This medium is used in quantitative (volumetric) estimations. The equivalent mass of  $KMnO_4$  in acidic medium is  $=\frac{Mol.\,mass}{5}$ . The oxidation reactions of acidified  $KMnO_4$  are catalysed by Mn (ii) ion.

The important oxidation reactions are:

(i) Ferrous salts are oxidised to ferric salts.

$$2KMnO_{4} + 3H_{2}SO_{4} \longrightarrow K_{2}SO_{4} + 2MnSO_{4} + 3H_{2}O + 5[O]$$

$$[2FeSO_{4} + H_{2}SO_{4} + [O] \longrightarrow Fe_{2}(SO_{4})_{3} + H_{2}O] \times 5$$

$$2KMnO_{4} + 10FeSO_{4} + 8H_{2}SO_{4} \longrightarrow 5Fe_{2}(SO_{4})_{3} + K_{2}SO_{4}$$

$$+ 2MnSO_{4} + 8H_{2}O$$
or 
$$2MnO_{4} + 10Fe^{2+} + 16H^{+} \longrightarrow 10Fe^{3+} + 2Mn^{2+} + 8H_{2}O$$

(ii) Iodine is evolved from potassium iodide.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$[2KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + I_2 + H_2O] \times 5$$

$$2KMnO_4+10KI+8H_2SO_4 \longrightarrow 6K_2SO_4+2MnSO_4+5I_2+8H_2O$$

or 
$$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

(iii) H<sub>2</sub>S is oxidised to sulphur.

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$$

(iv)  $SO_2$  is oxidised to  $H_2SO_4$ .

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

(v) Nitrites are oxidised to nitrates.

$$2KMnO_4 + 5KNO_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5KNO_3 + 3H_2O_4$$

(vi) Oxalic acid is oxidised to CO<sub>2</sub>.

$$\begin{array}{c} \text{COOH} \\ \text{5 I} \\ \text{COOH} \end{array} + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow \begin{array}{c} \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 \\ + 10\text{CO}_2 + 8\text{H}_2\text{O} \end{array}$$

(vii) It oxidises hydrogen halides (HCl, HBr or HI) into  $X_2$ (halogen).

$$2KMnO_4 + 3H_2SO_4 + 10HX \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O_7 + 5X_2$$

(viii) Arsenites are oxidised to arsenates.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$[\mathring{N}a_3AsO_3 + [O] \longrightarrow Na_3AsO_4] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5Na_3AsO_3 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Na_3AsO_4 + 3H_2O$$

(ix) Hydrogen peroxide is oxidised to  $H_2O$  and  $O_2$ .  $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$  $[H_2O_2 + [O] \longrightarrow H_2O + O_2] \times 5$ 

$$\begin{array}{c} 2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 \\ & + 8H_2O + 5O_2 \\ or \ 2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2 \\ (x) \ Ethyl \ alcohol \ is \ oxidised \ to \ acetaldehyde. \\ 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \\ \hline [C_2H_5OH + [O] \longrightarrow CH_3CHO + H_2O] \times 5 \\ \hline 2KMnO_4 + 3H_2SO_4 + 5C_2H_5OH \longrightarrow 5CH_3CHO + K_2SO_4 + 2MnSO_4 + 8H_2O \\ \hline \end{array}$$

#### ■ In Neutral Medium

(i) H<sub>2</sub>S is oxidised to sulphur.

$$2KMnO_4 + H_2O \longrightarrow 2MnO_2 + 2KOH + 3[O]$$
$$[H_2S+[O] \longrightarrow H_2O + S] \times 3$$

$$2KMnO_4 + 3H_2S \longrightarrow 2KOH + 2MnO_2 + 2H_2O + 3S$$

(ii) Manganese sulphate is oxidised to MnO2.

$$2KMnO_4 + H_2O \longrightarrow 2MnO_2 + 2KOH + 3[O]$$

$$[MnSO_4 + H_2O + [O] \longrightarrow MnO_2 + H_2SO_4] \times 3$$

$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$$

 $2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow K_2SO_4 + 5MnO_2 + 2H_2SO_4$ 

(iii) Sodium thiosulphate is oxidised to sulphate and sulphur.

$$2KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3Na_2SO_4 + 3S$$

#### In Alkaline Medium

(i) It oxidises iodide to iodate.

$$\begin{split} 2KMnO_4 + H_2O & \longrightarrow 2KOH + 2MnO_2 + 3[O] \\ KI + 3[O] & \longrightarrow KIO_3 \end{split}$$

$$2KMnO_4 + KI + H_2O \longrightarrow 2KOH + 2MnO_2 + KIO_3$$

(ii) It oxidises ethylene to ethylene glycol.

$$\begin{array}{ccc} CH_2 & CH_2OH \\ \parallel & +H_2O + [O] \longrightarrow | \\ CH_2 & CH_2OH \end{array}$$

In alkaline medium it is called Baeyer's reagent.

**Structure:** In permanganate ion, manganese undergoes  $sp^3$ -hybridisation *i.e.*, tetrahedral configuration results. Four oxygen atoms are present on the four apices of the tetrahedron.



#### Uses

(i) KMnO<sub>4</sub> is used as an oxidising agent in laboratory and industry. In volumetric estimations, the solution is first standardised before use. In volumetric estimations, acidified standardised KMnO<sub>4</sub> solution is used. For maintaining acidic medium only dilute H<sub>2</sub>SO<sub>4</sub> is used. HCl or HNO<sub>3</sub> are not used

because HCl reacts with KMnO<sub>4</sub> and produce Cl<sub>2</sub> gas while HNO<sub>3</sub>, itself reacts as an oxidising agent.

- (ii) Alkaline potassium permanganate is called Baeyer's reagent. This reagent is used in organic chemistry for the test of unsaturation. KMnO<sub>4</sub> is used in the manufacture of saccharin, benzoic acid, acetaldehyde, etc.
- (iii) KMnO<sub>4</sub> is used in qualitative analysis for detecting halides, sulphites, oxalates, etc.
- (iv) It is widely used as a disinfectant and germicide. A very dilute solution of  $KMnO_4$  is employed for washing wounds and gargling of mouth sores. It is also used for purifying well water.

## 14.8 POSITION OF IRON IN PERIODIC TABLE

Iron belongs to fourth period and VIII group of the extended form of periodic table. VIII group consists of nine elements arranged in three triads. Iron is a member of first triad and other two members of this triad are cobalt and nickel. These three metals are called **ferrous metals** and belong to first transition series (3d series) of the periodic table. The members of second and third triads are collectively known as **platinum metals** or **noble metals**.

Three elements iron, cobalt and nickel possess nearly the same atomic masses and resemble each other closely in their properties. The following discussion shows similarities and gradation in the properties of Fe, Co and Ni.

1. Electronic configuration: Two electrons are present in outermost shell while the penultimate shell is incomplete. The number of electrons on 3d-shell varies from 6 to 8.

Fe	26	2, 8, 14, 2	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6, 4s^2$ $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^7, 4s^2$	$[Ar](3d^64s^2)$
Co	27	2, 8, 15, 2	$1s^2, 2s^22p^6, 3s^23p^63d^7, 4s^2$	$[Ar](3d^74s^2)$
Ni	28	2, 8, 16, 2	$1s^2, 2s^22p^6, 3s^23p^63d^8, 4s^2$	$[Ar](3d^84s^2)$

Thus, the last differentiating electron is accommodated on 3d-shell. Hence, these elements are called transition elements or d-block elements.

**2. Valency:** They form 'ous' and 'ic' salts showing di- and trivalencies. The stability of  $M^{2+}$  cations increases from Fe<sup>2+</sup> to Ni<sup>2+</sup> ion. Thus, the reducing property of these is in the order Fe<sup>2+</sup>> Co<sup>2+</sup> > Ni<sup>2+</sup>. The removal of a 3d electron from  $M^{2+}$  cations to oxidise them into  $M^{3+}$  cations becomes more and more difficult as we move from Fe<sup>2+</sup> to Ni<sup>2+</sup>. Thus, the tendency to show trivalency decreases sharply from Fe to Ni, *i.e.*, stability of  $M^{3+}$  cations is in the order Fe<sup>3+</sup> > Co<sup>3+</sup> > Ni<sup>3+</sup>. The reason for more stability of Fe<sup>3+</sup> cations is that it has a half-filled 3d-orbitals.

Fe<sup>3+</sup> 2, 8, 8 +5 
$$3d^5$$
  $\uparrow$   $\uparrow$   $\uparrow$   $\uparrow$ 

 $\text{Co}^{3+}$  and  $\text{Ni}^{3+}$  have relatively unstable  $3d^6$  and  $3d^7$  configurations respectively.

Co <sup>3+</sup>	2, 8, 8 +6	$3d^6$	↑↓	1	↑·	<b>↑</b>	<b>↑</b>
Ni <sup>3+</sup>	2, 8, 8 +7	$3d^7$	↑↓	↑↓	1	1	1

Thus, in ous-series, nickelous compounds are most stable while in ic-series, ferric compounds are most stable.

**3. Occurrence:** All the three are relatively abundant. However, iron is more abundant than nickel and cobalt.

## ■ Physical Characteristics

(a) Physical state: These are all greyish white hard metals of high densities. The hardness and density increases from Fe to Ni.

Element	Fe	Co	Ni
Density	7.86	8.9	8.9

(b) Melting and boiling points: They have high melting and boiling points. This shows that covalent bonding is also present involving d electrons between atoms.

Element	. Fe	Co .	Ni
M.pt. (°C)	1536	1495	1453
B.pt. (°C)	3000	2900	2730

- (c) Ionisation energy: Ionisation energies are about the same. Hence, they have same tendency to form ions.
- **(d) Oxidation potential:** The values of oxidation potentials are fairly close to each other. The values are positive and hence they can liberate hydrogen from dilute acids.

Element	Fe	Co	Ni
First I.E. (eV)	7.90	7.86	7.63
Oxidation potential (Volt)	+0.44	+0.28	+0.25

- (e) Magnetic property: All the three elements are ferromagnetic, *i.e.*, these are strongly attracted by a magnet and remain magnetised even after the removal of the magnetic field. The ferromagnetic property decreases from iron to nickel.
- **(f) Catalytic property:** All the three elements are used as catalysts especially in the reactions involving the addition of hydrogen as they occlude or adsorb hydrogen.

# ■ Chemical Properties

The metals are reactive and their reactivity decreases from Fe to Ni.

(a) Action of air: Cobalt and nickel are not affected by air under ordinary conditions. However, iron is affected by moist air. The oxidation of iron into hydrated iron oxide,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , is termed rusting of iron.

When iron is strongly heated in air or oxygen, it forms ferroso-ferric oxide, Fe<sub>3</sub>O<sub>4</sub> (upto 500°C) and Fe<sub>2</sub>O<sub>3</sub> above 500°C. Cobalt when strongly heated also forms Co<sub>3</sub>O<sub>4</sub> while nickel forms NiO.

$$3\text{Fe} + 2\text{O}_2 \longrightarrow \text{Fe}_3\text{O}_4$$
  
 $2\text{Ni} + \text{O}_2 \longrightarrow 2\text{NiO}$ 

**(b)** Action of water: The metals are not affected by water under ordinary conditions but when steam is passed over hot metals, these get oxidised with evolution of hydrogen.

3Fe + 4H<sub>2</sub>O (steam) 
$$\longrightarrow$$
 Fe<sub>3</sub>O<sub>4</sub> + 4H<sub>2</sub>  
Co + H<sub>2</sub>O (steam)  $\longrightarrow$  CoO + H<sub>2</sub>  
Ni + H<sub>2</sub>O (steam)  $\longrightarrow$  NiO + H<sub>2</sub>

(c) Action of acids: Non-oxidising acids (dilute HCl and dilute H<sub>2</sub>SO<sub>4</sub>) evolve hydrogen with iron, cobalt and nickel. Iron reacts readily while cobalt and nickel react slowly.

$$M + 2HCl \longrightarrow MCl_2 + H_2$$
  
 $M + H_2SO_4 \longrightarrow MSO_4 + H_2$ 

All the three metals, dissolve in concentrated sulphuric acid evolving sulphur dioxide.

$$2Fe + 6H2SO4 \longrightarrow Fe2(SO4)3 + 3SO2 + 6H2O$$

$$Co + 2H2SO4 \longrightarrow CoSO4 + SO2 + 2H2O$$

$$Ni + 2H2SO4 \longrightarrow NiSO4 + SO2 + 2H2O$$

These metals dissolve in dilute HNO3 evolving NO.

$$[M + 2HNO_3 \longrightarrow M(NO_3)_2 + 2H] \times 3$$

$$[3H + HNO_3 \longrightarrow NO + 2H_2O] \times 2$$

$$3M + 8HNO_3 \longrightarrow 3M(NO_3)_2 + 2NO + 4H_2O$$

However, with concentrated nitric acid, these metals become passive.

- (d) Action of alkalies: These metals are not affected by
- (e) Action of halogens: These metals directly combine with halogens.

$$\begin{array}{ccc} \text{2Fe} + 3\text{Cl}_2 & \longrightarrow & 2\text{FeCl}_3 \\ & \text{Ferric chloride} \\ \text{Co} + \text{Cl}_2 & \longrightarrow & \text{CoCl}_2 \\ & \text{Cobaltous chloride} \\ \text{Ni} + \text{Cl}_2 & \longrightarrow & \text{NiCl}_2 \\ & \text{Nickelous chloride} \\ \end{array}$$

FeI<sub>3</sub> is unstable and gets reduced to FeI<sub>2</sub>.

$$2\text{FeI}_3 \longrightarrow 2\text{FeI}_2 + \text{I}_2$$

(f) Action of carbon monoxide: All the three metals, combine with carbon monoxide to form volatile carbonyls, viz., Fe(CO)<sub>5</sub>, Co<sub>2</sub>(CO)<sub>8</sub> and Ni(CO)<sub>4</sub>.

$$Ni + 4CO \longrightarrow Ni(CO)_4$$

(g) Isomorphous sulphates: All form isomorphous sulphates.

All these sulphates form double sulphates which are also isomorphous. For example,  $(NH_4)_2SO_4$ ·FeSO<sub>4</sub>·6H<sub>2</sub>O Mohr's salt and  $(NH_4)_2SO_4$ ·NiSO<sub>4</sub>·6H<sub>2</sub>O nickel ammonium sulphate are isomorphous.

(h) Complex compounds: All form complex salts. Some examples are given below:

$$K_4Co(CN)_6$$
  
Potassium cobaltocyanide  $K_3Co(NO_2)_6$   
Potassium cobaltinitrite

Nickel has a coordination number 4 or 6 whereas, iron and cobalt show a coordination number 6 only. Iron does not form amine complex while nickel and cobalt form amine complexes such as [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> and [Ni(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>.

- (i) Alloy formation: All the three elements have great tendency to form alloys with each other and with other metals.
- (j) Colour of the compounds: The compounds of iron, cobalt and nickel are coloured as 3d-energy shell is incomplete in  $M^{2+}$  and  $M^{3+}$  cations.

Ferrous compounds are usually green while ferric compounds are yellow. The colour of nickel compounds is green while of cobalt compounds is pink.

# 14.9 EXTRACTION OF IRON

Occurrence: Iron is the fourth most abundant element and the second most abundant metal in nature. It occurs in combined state. The main ores of iron are:

- 1. Oxide ores:
- (i) Magnetite, Fe<sub>3</sub>O<sub>4</sub>. It is usually black in colour. It is richest ore of iron and contains upto 70% of the metal.
  - (ii) Haematite, Fe<sub>2</sub>O<sub>3</sub>. It is usually red in colour.
- (iii) Limonite or hydrated ferric oxide, Fe<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O. It has yellow, brown or red colour.
  - 2. Carbonate ore:

Siderite or Sepathic iron, FeCO<sub>3</sub>. It is also called clayiron stone due to the presence of excess of clay in it.

- 3. Sulphide ores:
- (i) Iron pyrites, FeS<sub>2</sub>. It is mainly used for the manufacture of sulphur dioxide (sulphuric acid). It is not used for extraction of iron.
- (ii) Chalcopyrites, CuFeS<sub>2</sub>. It is used for the extraction of copper.

Iron ores have been reported at many places especially in England, Sweden, Germany, U.S.A., Russia, Belgium, France, Canada and India. Huge deposits of red haematite are available in India in Mayurbhanj (Orissa), Singhbhum (Jharkhand), Madhya Pradesh and Mysore (Karnataka). On the whole, India possesses about one fourth of the total world reserves of iron ore.

Iron is extracted from its oxide ores especially from the magnetite, haematite and limonite ores. The extraction involves the following steps:

- (i) Concentration of ore: The concentration of ore is done by gravity process. The ore is crushed to small pieces and washed with water to remove silicious impurities. The washed ore is then subjected to electromagnetic separation.
- (ii) Calcination and roasting: The concentrated ore is heated in excess of air. This treatment produces the following results.
  - (a) Moisture and carbon dioxide are removed.

$$2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \longrightarrow 2\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$$
  
 $\text{Fe}\text{CO}_3 \longrightarrow \text{Fe}\text{O} + \text{CO}_2$ 

(b) Sulphur, phosphorus, arsenic, etc., are oxidised to their oxides and are, thus, removed as volatile gases.

$$S + O_2 \longrightarrow SO_2$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

$$4As + 3O_2 \longrightarrow 2As_2O_3$$

(c) Ferrous oxide is oxidised to ferric oxide.

$$2\text{FeO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{Fe}_2\text{O}_3$$

- (d) The entire mass becomes porous.
- (iii) Smelting: The calcined ore is mixed with limestone  $(CaCO_3)$  and coke in the ratio of 8:1:4 and introduced in a blast furnace for smelting.

#### Blast Furnace

Blast furnace is a chimney like tall steel structure lined with fire bricks, 25–60 metre high and 8–10 metre in diameter at its widest part (Fig. 14.2). The furnace has three main parts:

- (1) A double cup and cone arrangements: At the top, the furnace has a hopper which rests over a cup and cone arrangement. By this arrangement charge is introduced into the furnace and also the arrangement prevents the exit of gases during charging.
- (2) **Shaft:** It is formed by joining two cones, the upper one is called the body and the lower one is called bosh. At the upper part, there is a hole, through which the hot burnt mixture of waste gases escape. In the lower part, there are openings for the insertion of water cooled pipes called *tuyeres* through which a blast of hot air is sent upward in the furnace.
- (3) **Hearth:** This is the lowest part of the furnace and serves as a large crucible. It is provided with two holes one for the removal of slag and other for molten metal.

Theory of reduction of oxide ore of iron—see chapter 4.

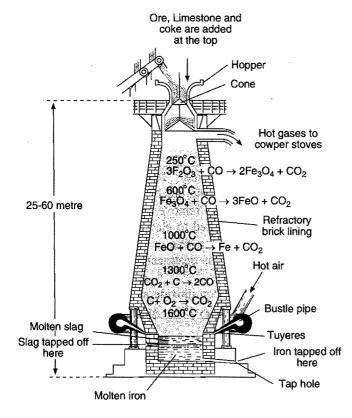


Fig. 14.2 Blast furnace for the manufacture of cast iron

The charge is introduced in the furnace by lowering the cup and cone arrangement and at the same time the furnace is lit and a blast of hot air is sent upwards through the *tuyeres*. The temperature varies from 1600°C to 250°C in the furnace from bottom to top. On the basis of variation in temperature, there are four zones where different chemical changes occur. The four zones are:

1. Combustion zone: This is the lowest part of the furnace above hearth where the temperature is about 1500°–1600°C. In this zone carbon burns in presence of hot air producing carbon dioxide and a lot of heat.

$$C + O_2 \longrightarrow CO_2 + 97.0$$
 kcals.

Carbon dioxide rises upwards and meets with red hot coke. It is reduced to carbon monoxide.

$$CO_2 + C \xrightarrow{1500^{\circ}C} 2CO$$

**2. Reduction zone:** This is the uppermost part of the furnace. The temperature varies from 250°C to 700°C. The oxide ore is reduced to iron in this zone. The reduction takes place through the following stages:

$$3Fe_2O_3 + CO \xrightarrow{300-400^{\circ}C} 2Fe_3O_4 + CO_2$$
 $Fe_3O_4 + CO \xrightarrow{500-600^{\circ}C} 3FeO + CO_2$ 
 $FeO + CO \xrightarrow{700^{\circ}C} Fe + CO_2$ 

However, the oxide ore which escapes reduction, gets completely reduced by carbon above 850°C.

Iron formed is called spongy iron. In the reduction reactions, heat is also evolved which decomposes part of carbon monoxide into carbon.

$$2CO \xrightarrow[iron]{Hot spongy} CO_2 + C$$

**3. Slag formation zone:** This is the central zone where the temperature varies from 800–1000°C. The limestone present in the charge decomposes into calcium oxide and carbon dioxide.

$$CaCO_3 \xrightarrow{1000^{\circ}C} CaO + CO_2$$

The calcium oxide acts as a flux as it combines with silica present as an impurity (gangue) to form a fusible slag of CaSiO<sub>3</sub>.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

Silicates, phosphates and manganates present as impurities in ore, are reduced to Si, P and Mn, respectively.

$$\begin{array}{c} P_4O_{10} + 10C \longrightarrow 4P + 10CO \\ SiO_2 + 2C \longrightarrow Si + 2CO \\ MnO_2 + 2C \longrightarrow Mn + 2CO \end{array}$$

These are partly absorbed by iron (spongy) and partly by slag.

$$2Ca_3(PO_3)_2 + 3SiO_2 + 10C \longrightarrow 3(2CaO \cdot SiO_2) + 4P + 10CO$$
  
 $3Fe + P \longrightarrow Fe_3P$ 

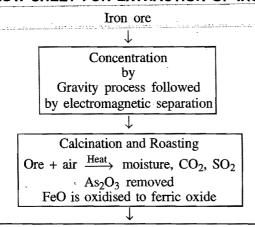
**4. Zone of fusion:** This is a zone just above the zone of combustion. The temperature ranges between 1200–1500°C. The spongy iron which has absorbed already C, Si, P, Mn, etc., melts at 1300°C and collects at the bottom of the hearth.

The slag which being lighter floats over the molten iron and prevents the oxidation of molten metal. The slag and molten metal are removed from their respective holes. The molten metal is run into moulds and is allowed to solidify.

Iron obtained from the blast furnace is called **pig iron.** It contains 93% iron, 5% carbon and rest silicon, manganese, phosphorus, etc., as impurities. The pig iron is remelted and cast or poured into moulds. This is known as cast iron. Hence, after remelting the pig iron becomes cast iron.

When the molten pig iron is cooled at once, the iron is called white cast iron, which contains carbon in the form of cementite, Fe<sub>3</sub>C and when the molten pig iron is cooled slowly and slowly, the iron is called as grey cast iron, which contains carbon in the form of graphite.

#### FLOW SHEET FOR EXTRACTION OF IRON



Smelting in a blast furnace (ore + coke + limestone). The following reactions occur.

Fe<sub>2</sub>O<sub>2</sub> +  $\frac{400 - 700^{\circ}\text{C}}{2}$  2Fe +  $\frac{3}{2}$ CO<sub>2</sub>

Fe<sub>2</sub>O<sub>3</sub> + 3CO 
$$\xrightarrow{400-700^{\circ}\text{C}}$$
 2Fe + 3CO<sub>2</sub> Spongy iron

CaCO<sub>3</sub>  $\xrightarrow{1000^{\circ}\text{C}}$  CaO + CO<sub>2</sub>
CaO + SiO<sub>2</sub>  $\longrightarrow$  CaSiO<sub>3</sub> (slag)

2CO  $\xrightarrow{\text{Hot iron}}$  CO<sub>2</sub> + C

SiO<sub>2</sub> + 2C  $\xrightarrow{1200^{\circ}\text{C}}$  Si + 2CO

MnO<sub>2</sub> + 2C  $\longrightarrow$  Mn + 2CO

P<sub>4</sub>O<sub>10</sub> + 10C  $\longrightarrow$  4P + 10CO

Spongy iron + C, Mn, Si, etc.  $\longrightarrow$  Impure iron

C·+ O<sub>2</sub>  $\xrightarrow{1600^{\circ}\text{C}}$  CO<sub>2</sub>

CO<sub>2</sub> + C  $\xrightarrow{1500^{\circ}\text{C}}$  2CO

(Fe = 93%; C = 5% and impurities of Mn, P, Si, etc. = 2%)

Cast iron

Pig iron

Remelted

and cooled

# 14.10 TYPES OF IRON

There are three commercial varieties of iron depending on their carbon content.

## (i) Cast Iron

It is the most impure form of iron and contains the highest percentage of carbon from 2.5 to 5 per cent and about 2 per cent of other impurities like Si, P, Mn and S. Cast iron is of two types:

- (a) White cast iron: Carbon is present in the form of cementite, Fe<sub>3</sub>C.
- (b) Grey cast iron: Carbon is present in the form of graphite. Cast iron melts at about 1250°C (due to presence of impurities) whereas pure iron melts at 1530°C. The molten cast iron expands on solidification and hence it produces good castings. Various articles such as stoves, pipes, radiators, railway sleepers, gutter pipes, toys, etc., are prepared from cast iron. Cast iron does not rust easily and neither be tempered. Due to high carbon content, it is hard and brittle and cannot be welded. It has very little ductility and thus cast iron is not suitable for forging.

## **(ii) Wrought Iron**

It is the purest form of iron. It contains the lowest percentage of carbon from 0.1 to 0.25 per cent and 0.3 per cent other impurities. It is manufactured from cast iron by **puddling process.** 

Wrought iron is manufactured in a special type of reverberatory furnace called puddling furnace, the hearth of which is lined with haematite, Fe<sub>2</sub>O<sub>3</sub>. The cast iron is melted on the hearth of the furnace by the hot gases and stirred with long iron rods. The impurities of cast iron are rapidly oxidised by oxygen of haematite (lining). Oxides of carbon and sulphur being volatile escape while those of Mn, P and Si form slag.

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO$$

$$3Si + 2Fe_2O_3 \longrightarrow 3SiO_2 + 4Fe$$

$$3Mn + Fe_2O_3 \longrightarrow 3MnO + 2Fe$$

$$MnO + SiO_2 \longrightarrow MnSiO_3 \text{ (Slag)}$$

$$6P + 5Fe_2O_3 \longrightarrow 3P_2O_5 + 10Fe$$

$$P_2O_5 + Fe_2O_3 \longrightarrow 2FePO_4 \text{ (Slag)}$$

With the removal of impurities, the melting point of the metal rises and it becomes a semi-solid mass. The semi-solid mass is taken out in the form of balls and is beaten under steam hammers to squeeze out as much of slag as possible. This produces almost pure iron known as wrought iron.

# ■ Properties

(i) Wrought iron is extremely tough, highly malleable and ductile. (ii) It softens at about 1000°C and then it can be forged and welded. (iii) On account of the presence of very small percentage of slag, it has fibrous structure and thus, can withstand high stresses. (iv) Wrought iron is resistant towards rusting and corrosion.

#### **■** Uses

It is used to make chains, nails, hooks, bolts, agricultural implements, electromagnets, bars, wires, etc.

## (iii) Steel

This is the most important commercial variety of iron. The percentage of carbon in this form of iron is midway between that of cast iron and wrought iron, *i.e.*, 0.25 to 2 per cent. There are many varieties of steel depending on the amount of carbon present in it.

- (a) Mild steels: These contain low percentage of carbon. Such steels show the properties of wrought iron along with elasticity and hardness.
- **(b) Hard steels:** These contain high percentage of carbon. They are hard and brittle.
- (c) Special steels or alloy steels: Steel mixed with small amount of nickel, cobalt, chromium, tungsten, molybdenum, manganese, etc., acquires special properties. Such products are called special steels or alloy steels. Some important alloy steels are listed below:

Name of the alloy steel	Metal added	Properties	Uses
1. Invar	36% Ni	Coefficient of expansion is very small	Measuring tapes, pendulums
2. Chromevan- adium steel	1% Cr; 0.15%V	High tensile strength	Springs, shafts, axles
3. Manganese steel	12-15% Mn	Hard and tough	Rock crushing machinery, almirah, helmets
4. Stainless steel	11.5% Cr; 2% Ni	Resists corrosion	Common articles
5. Tungsten steel	14–20% W; 3–8% Cr	Very hard	High speed tools
6. Alnico	60% Fe, 12% Al, 20% Ni, 8% Co	Highly magnetic	For making perma- nent magnets
7. Permalloy	21% Fe, 78% Ni and carbon	Strongly magne- tised by electric current, loses magnetism when current is cut off.	For making electromagnets, ocean cables, etc.

#### Manufacture of Steel

Many methods are used for the manufacture of steel. Some are described below:

(i) The Bessemer's process: The process is based on the fact that impurities of pig iron are completely oxidised in presence of hot air blast, *i.e.*, virtually wrought iron is obtained. This is then mixed with a known amount of *spiegeleisen*, an alloy of iron, manganese and carbon to obtain steel.

The process is carried out in Bessemer converter lined with silica bricks. The molten pig iron is introduced in the converter

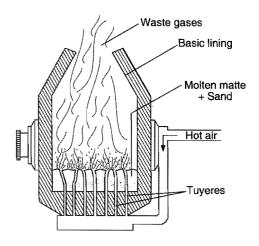


Fig. 14.3

and a blast of hot air is blown through it from the bottom and keeping the mouth of the converter vertically upwards. Silica and manganese present in pig iron are first oxidised and then combine to form slag.

$$Si + O_2 \longrightarrow SiO_2$$
  
 $2Mn + O_2 \longrightarrow 2MnO$   
 $MnO + SiO_2 \longrightarrow MnSiO_3$ 

In the end, carbon is oxidised to carbon monoxide which burns with blue flame at the mouth of the converter. Some iron is also oxidised which converts the carbon into carbon monoxide.

$$4\text{Fe} + 3\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3$$
  
 $\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 2\text{Fe} + 3\text{CO}$ 

When whole of the carbon is oxidised, the blue flame suddenly dies out. The air supply is stopped for a while and the requisite amount of *spiegeleisen* is added. The blast is continued just for a moment to ensure complete mixing. The resulting product is the manganese steel.

When cast iron or pig iron contains phosphorus as an impurity, a basic lining of CaO or MgO is used in the Bessemer converter. Phosphorus is oxidised to  $P_4O_{10}$  which combines with CaO to form calcium phosphate as slag.

$$\begin{array}{c} \text{4P} + 5\text{O}_2 \longrightarrow \text{P}_4\text{O}_{10} \\ \text{6CaO} + \text{P}_4\text{O}_{10} \longrightarrow 2\text{Ca}_3(\text{PO}_4)_2 \end{array}$$

This slag is used as a fertilizer and known as Thomas slag.

(ii) Open hearth process or Siemens-Martin process: This is the modern process and the furnace used consists of an open hearth. The hearth is lined with silica or calcined dolomite (CaO·MgO) depending upon the nature of impurities present in pig or cast iron. Silica lining is used if the impurities are manganese, silicon, etc., and calcined dolomite lining is used if much of phosphorus is present. A high temperature of about 1500°C is generated by burning producer gas which works on regenerative system of heat economy (Fig. 14.4).

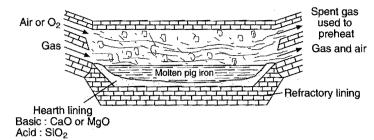


Fig. 14.4

The charge consists of pig or cast iron, iron scrap, iron ore (haematite) and lime. The charge is heated on the hearth of the furnace. The impurities are oxidised by iron ore.

$$3Si + 2Fe_2O_3 \longrightarrow 4Fe + 3SiO_2$$

$$3Mn + Fe_2O_3 \longrightarrow 2Fe + 3MnO$$

$$MnO + SiO_2 \longrightarrow MnSiO_3 \text{ (Slag)}$$

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO$$

$$12P + 10Fe_2O_3 \longrightarrow 3P_4O_{10} + 20Fe$$

$$6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2 \text{ (Slag)}$$

$$CaO + SiO_2 \longrightarrow CaSiO_3 \text{ (Slag)}$$

$$2Fe_2O_3 + 3S \longrightarrow 3SO_2 + 4Fe$$

Samples of steel are drawn from time to time and tested for carbon content. Finally *spiegeleisen* (an alloy of iron, manganese and carbon) is added to the molten mass to obtain desired steel. The process takes about 8 to 10 hours for completion. The process takes longer time than Bessemer's process but it has following advantage over the Bessemer's process.

- (a) The temperature can be controlled as the heating is done externally.
- (b) As it is a slower process, it can be controlled in better way. The composition and quality can be well controlled.
- (c) The loss of iron in this process is only 4% while the loss is about 15% in Bessemer's process.
  - (d) In this process scrap iron is reused.
  - (e) This yields better quality of steel.
- (f) A considerable economy of the fuel is achieved by using the regenerative system.

(iii) The electric process: This process is similar to open hearth process with a difference that heating is done electrically. The steel of much better quality can be obtained but the process is rather costly.

The process consists in heating of the charge having pig or cast iron, scrap iron, iron ore (haematite) and lime in an electric furnace using vertical carbon electrodes. When the arc is struck between the electrodes, the high temperature of about 2000°C generated melts the charge and chemical reactions start instantaneously. The impurities are oxidised by iron ore in the same fashion as in the open hearth process.

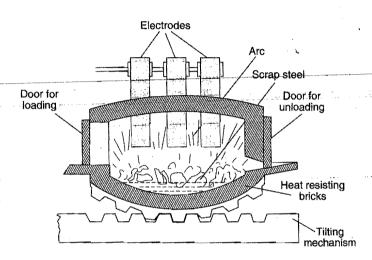


Fig. 14.5

This method is especially useful for the production of the alloy steels.

#### Heat Treatment of Steels

The properties of steel depend on three factors:

(i) Carbon content: With the increase of carbon content the hardness and tensile strength of the steel increases while ductility decreases.

#### COMPARISON OF CAST IRON, WROUGHT IRON AND STEEL

	Property	Cast iron	Wrought iron	Steel
1.	Chemical composition	Iron 93–95%	Iron 99.5-99.8%	Iron 98–99.5%
		Carbon 2.5-5%	Carbon 0.1-0.21%	Carbon 0.25 to 2.0%
	·	Impurities about 2%	Impurities about 0.3%	
2.	Melting point	Lowest about 1200°C	Highest about 1500°C	Between 1300-1400°C
3.	Hardness	Very hard	Soft	Medium hardness
4.	Malleability	Brittle	Malleable	Malleable and brittle
5.	Welding	Cannot be welded	Can be welded easily	Can be welded with difficulty
6.	Tempering	Cannot be tempered	Cannot be tempered	Can be tempered
7.	Magnetisation	Cannot be permanently magnetised	Magnetisation is not permanent but easy	Can be permanently magnetised
8.	Structure	Crystalline	Fibrous	Granular

- (ii) Presence of other metals: The presence of Si gives steel a fibrous structure. Presence of Mn produces elasticity and increases tensile strength. Cr imparts resistance to chemical action.
- (iii) Heat treatment: The hardness and elasticity of the steel can be changed by heating the steel at different temperatures and then allowing to cool it in different ways. The following heat treatments are given to steel:
- (a) Annealing: It is a process of heating steel to bright redness and then cooling it very slowly. This treatment makes the steel soft and ductile. This type of steel is used in fabrication process.
- (b) Quenching: It is a process of heating steel to bright redness and then cooling it suddenly by plunging it in water or oil. Such a steel is extremely hard and brittle. It has very low elasticity.
- (c) **Tempering:** It is a process of heating the quenched steel to a temperature much below redness and then cooling it slowly. Such steel is neither so hard nor so brittle. In the process of tempering, a thin film of the oxide is formed on the surface of steel. The colour of the oxide film depends on the temperature at which the quenched steel is heated.

Temperature range	Colour of the oxide film
200-230°C	Yellow
225–270°C	Brown
300℃	Blue

The surface treatment of the steel is done by the following two processes:

- (a) Case hardening: The process of producing a thin coating of hardened steel on the surface of the mild steel is called case hardening. This is done by heating the mild steel with charcoal and then plunging into oil. This produces a thin coating of hardened steel on the surface. Such a steel becomes resistant to wear and tear.
- **(b) Nitriding:** The process of producing a hard coating of iron nitride on the surface of steel is called nitriding. Steel is heated in the atmosphere of dry ammonia at 500–600°C for about 3 to 4 days when a hard coating of iron nitride is produced on the surface.

# 14.11 PASSIVITY OF IRON

The following are the common properties of iron.

- (a) It evolves hydrogen gas, when made to react with dilute HCl or dilute  $H_2SO_4$ .
- (b) It precipitates silver from silver nitrate solution and copper from copper sulphate solution.

But if a piece of iron is first dipped in concentrated nitric acid for sometime and then made to react with the above reagents, neither hydrogen is evolved nor silver or copper are precipitated. Thus, iron by treatment with concentrated nitric acid has lost its usual properties or it has been rendered inert or passive. Such behaviour is not only shown by iron but also by many other metals like Cr, Co, Ni, Al, etc. This phenomenon is known as passivity and the chemical substances which bring passivity are called passivators.

"The inertness exhibited by metals under conditions when chemical activity is to be expected is called chemical passivity." Iron can be rendered passive by other oxidising agents like chromic acid, KMnO<sub>4</sub>, conc. H<sub>2</sub>SO<sub>4</sub>, etc. The passivity of the iron is believed to be due to formation of an extremely thin film (invisible) of oxide on the surface of iron. Passive iron can be made active by scratching or heating in a reducing atmosphere of H<sub>2</sub> or CO, or heating in HNO<sub>3</sub> upto 75°C.

# 14.12 COMPOUNDS OF IRON

## Ferrous Sulphate (Green vitriol), FeSO<sub>4</sub>·7H<sub>2</sub>O

This is the best known ferrous salt. It occurs in nature as *copperas* and is formed by the oxidation of pyrites under the action of water and atmospheric air.

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

It is commonly known as harakasis.

**Preparation.** (i) It is obtained by dissolving scrap iron in dilute sulphuric acid.

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

The solution is crystallised by the addition of alcohol as ferrous sulphate is sparingly soluble in it.

(ii) It can also be prepared in the laboratory from the Kipp's waste. The excess of sulphuric acid is neutralised by heating with a small quantity of iron fillings. The solution is then crystallised.

Manufacture: Commercially, ferrous sulphate is obtained by the slow oxidation of iron pyrites in the presence of air and moisture. The pyrites are exposed to air in big heaps.

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4$$

The free sulphuric acid is removed by the addition of scrap iron. On crystallisation green crystals are obtained.

## **■** Properties

(i) Hydrated ferrous sulphate (FeSO<sub>4</sub>·7H<sub>2</sub>O) is a green crystalline compound. Due to atmospheric oxidation, the crystals acquire brownish-yellow colour due to formation of basic ferric sulphate.

$$4\text{FeSO}_4 + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{Fe(OH)} \cdot \text{SO}_4$$
Basic ferric sulphate

(ii) Action of heat: At 300°C, it becomes anhydrous. The anhydrous ferrous sulphate is colourless. The anhydrous salt when strongly heated, breaks up to form ferric oxide with the evolution of SO<sub>2</sub> and SO<sub>3</sub>.

$$FeSO_{4} \cdot 7H_{2}O \xrightarrow[-7H_{2}O]{300^{\circ}C} 2FeSO_{4} \xrightarrow[\text{White}]{High} Fe_{2}O_{3} + SO_{2} + SO_{3}$$

(iii) The aqueous solution of ferrous sulphate is slightly acidic due to its hydrolysis.

$$FeSO_4 + 2H_2O \rightleftharpoons Fe(OH)_2 + H_2SO_4$$
  
Weak base Strong acid

- (iv) Ferrous sulphate is a strong reducing agent.
- (a) It decolourises acidified potassium permanganate.  $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$  $[2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5$

$$10\text{FeSO}_4 + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 \longrightarrow 5\text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O}_4$$

(b) It turns potassium dichromate (acidified) green as dichromate is reduced to chromic salt (green).

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$= \underbrace{[2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 3}_{CF_2O_2 \longrightarrow Fe_2$$

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O_4$$

(c) It reduces gold chloride to gold.

$$AuCl_3 + 3FeSO_4 \longrightarrow Au + Fe_2(SO_4)_3 + FeCl_3$$

(d) It reduces mercuric chloride to mercurous chloride.

$$[2HgCl2 \longrightarrow Hg2Cl2 + 2Cl] \times 3$$

$$[3FeSO4 + 3Cl \longrightarrow Fe2(SO4)3 + FeCl3] \times 2$$

$$6HgCl_2 + 6FeSO_4 \longrightarrow 3Hg_2Cl_2 + 2Fe_2(SO_4)_3 + 2FeCl_3$$

(v) A cold solution of ferrous sulphate absorbs nitric oxide forming dark brown addition compound, nitroso ferrous sulphate.

The NO gas is evolved when the solution is heated.

- (vi) It forms double sulphates of the composition  $R_2SO_4$ ·FeSO<sub>4</sub>·6H<sub>2</sub>O where R = an alkali metal or NH<sub>4</sub><sup>+</sup> radical. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·FeSO<sub>4</sub>·6H<sub>2</sub>O (ferrous ammonium sulphate) is known as Mohr's salt.
- (vii) It combines with potassium cyanide (excess) forming potassium ferrocyanide, K<sub>4</sub>Fe(CN)<sub>6</sub>.

$$FeSO_4 + 2KCN \longrightarrow Fe(CN)_2 + K_2SO_4$$

$$Fe(CN)_2 + 4KCN \longrightarrow K_4Fe(CN)_6$$

$$FeSO_4 + 6KCN \longrightarrow K_4Fe(CN)_6 + K_2SO_4$$

#### Uses

(i) Ferrous sulphate is used for making blue black ink. The ink is prepared by mixing a solution of tannin and ferrous sulphate. A colourless iron salt of tannic acid is formed. A blue dye (usually indigo) is added. The writing with this ink is blue but soon on exposure to air, it becomes black on account of oxidation of colourless ferrous salt into black ferric salt.

- (ii) It is used as a mordant in dyeing.
- (iii) It is also used as an insecticide in agriculture.
- (iv) It is employed as a laboratory reagent and in the preparation of Mohr's salt.

## Ferrous Ammonium Sulphate (Mohr's salt) (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·FeSO<sub>4</sub>·6H<sub>2</sub>O

**Preparation:** The double salt is best prepared by making saturated solutions of pure ferrous sulphate and pure ammonium sulphate in air free distilled water at 40°C. Both the solutions are mixed and allowed to cool. Generally, few drops of sulphuric acid and a little iron wire are added before crystallisation as to prevent oxidation of ferrous sulphate into ferric sulphate. The salt is obtained as pale green crystals.

### Properties

It is pale green crystalline compound which does noteffloresce like ferrous sulphate. It is less readily oxidised in the solid state. It is, therefore, a better volumetric reagent in preference to ferrous sulphate. Chemically, it is similar to ferrous sulphate. All the chemical reactions observed in the case of ferrous sulphate are given by ferrous ammonium sulphate.

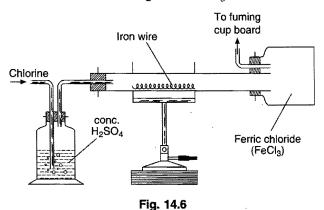
## Ferric Chloride, FeCl<sub>3</sub>

This is the most important ferric salt. It is known in anhydrous and hydrated forms. The hydrated form consists of six water molecules, FeCl<sub>3</sub>·6H<sub>2</sub>O.

**Preparation:** (i) Anhydrous ferric chloride is obtained by passing dry chlorine gas over heated iron fillings (Fig. 14.6).

The vapours are condensed in a bottle attached to the outlet of the tube.

$$2\text{Fe} + 3\text{Cl}_2 \longrightarrow 2\text{FeCl}_3$$



(ii) Hydrated ferric chloride is obtained by the action of hydrochloric acid on ferric carbonate, ferric hydroxide or ferric oxide.

$$Fe_{2}(CO_{3})_{3} + 6HCl \longrightarrow 2FeCl_{3} + 3H_{2}O + 3CO_{2}$$

$$Fe(OH)_{3} + 3HCl \longrightarrow FeCl_{3} + 3H_{2}O$$

$$Fe_{2}O_{3} + 6HCl \longrightarrow 2FeCl_{3} + 3H_{2}O$$

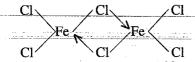
The solution on evaporation and cooling deposits yellow crystals of hydrated ferric chloride, FeCl<sub>3</sub>·6H<sub>2</sub>O.

## ■ Properties

(i) Anhydrous ferric chloride is a dark red deliquescent solid. It is sublimed at about 300°C and its vapour density corresponds to dimeric formula, Fe<sub>2</sub>Cl<sub>6</sub>. The dimer dissociates at high temperatures to FeCl<sub>3</sub>. The dissociation into FeCl<sub>3</sub> is complete at 750°C. Above this temperature it breaks into ferrous chloride and chlorine.

Fe<sub>2</sub>Cl<sub>6</sub> 
$$\stackrel{750^{\circ}\text{C}}{\rightleftharpoons}$$
 2FeCl<sub>3</sub>  $\stackrel{\text{Above 750^{\circ}\text{C}}}{\rightleftharpoons}$  2FeCl<sub>2</sub> + Cl<sub>2</sub>

(ii) Anhydrous ferric chloride behaves as a covalent compound as it is soluble in non-polar solvents like ether, alcohol, etc. It is represented by chlorine bridge structure.



(iii) It dissolves in water. The solution is acidic in nature due to its hydrolysis as shown below:

$$FeCl_3 + 3HOH \Longrightarrow Fe(OH)_3 + 3HCl$$

The solution is stabilised by the addition of hydrochloric acid to prevent hydrolysis.

(iv) Anhydrous ferric chloride absorbs ammonia.

$$FeCl_3 + 6NH_3 \longrightarrow FeCl_3 \cdot 6NH_3$$

- (v) Ferric chloride acts as an oxidising agent.
- (a) It oxidises stannous chloride to stannic chloride.

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

(b) It oxidises SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>.

$$2\text{FeCl}_3 + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{FeCl}_2 + \text{H}_2\text{SO}_4 + 2\text{HCl}$$

(c) It oxidises H<sub>2</sub>S to S.

or

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$$

(d) It liberates iodine from KI.

$$2FeCl_3 + 2KI \longrightarrow 2FeCl_2 + 2KCl + I_2$$

(e) Nascent hydrogen reduces FeCl<sub>3</sub> into FeCl<sub>2</sub>.

$$FeCl_3 + H \longrightarrow FeCl_2 + HCl$$

(vi) When ammonium hydroxide is added to the solution of ferric chloride, a reddish-brown precipitate of ferric hydroxide is formed.

$$FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 + 3NH_4Cl$$

(vii) When a solution of thiocyanate ions is added to ferric chloride solution, a deep red colouration is produced due to formation of a complex salt.

FeCl<sub>3</sub> + NH<sub>4</sub>CNS 
$$\longrightarrow$$
 Fe(SCN)Cl<sub>2</sub> + NH<sub>4</sub>Cl  
FeCl<sub>3</sub> + 3NH<sub>4</sub>CNS  $\longrightarrow$  Fe(SCN)<sub>3</sub> + 3NH<sub>4</sub>Cl

(viii) Ferric chloride forms a complex, prussian blue with potassium ferrocyanide.

$$4\text{FeCl}_3 + 3\text{K}_4\text{Fe}(\text{CN})_6 \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl}$$
Prussian blue
(Ferri ferrocyanide)

(ix) On heating hydrated ferric chloride FeCl<sub>3</sub>·6H<sub>2</sub>O, anhydrous ferric chloride is not obtained. It is changed to Fe<sub>2</sub>O<sub>3</sub> with evolution of H<sub>2</sub>O and HCl.

$$2[FeCl_3 \cdot 6H_2O] \xrightarrow{Heat} Fe_2O_3 + 6HCl + 9H_2O$$

Hydrated ferric chloride may be dehydrated by heating with thionyl chloride.

$$FeCl_3 \cdot 6H_2O + 6SOCl_2 \longrightarrow FeCl_3 + 12HCl + 6SO_2$$

#### **■** Uses

(i) The alcoholic solution is used in medicine under the name tincture ferri perchloride. (ii) It is used as a laboratory reagent in the detection of acetates and phenols and also as an oxidising agent. (iii) It is used for making prussian blue.

# 14.12 CORROSION OF IRON

Corrosion is defined as the gradual transformation of a metal into its combined state because of the reaction with the environment. Metals are usually extracted from their ores. Nature tries to convert them again into the ore form. The process by which the metals have the tendency to go back to their combined state, is termed corrosion.

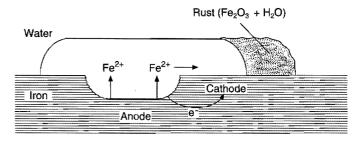


Fig. 14.7

When iron is exposed to moist air, it is found covered with a reddish-brown coating which can easily be detached. The reddish-brown coating is called 'rust'. Thus, the corrosion of iron or formation of the rust is called **rusting.** The composition of the rust is not certain but it mainly contains hydrated ferric oxide,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , together with a small quantity of ferrous carbonate. The rust is formed by the action of water on iron in presence of dissolved oxygen and carbon dioxide. It has been observed that impure iron is more prone to rusting.

The following are the favourable conditions for the rusting of iron:

- (i) Presence of moisture
- (ii) Presence of a weakly acidic atmosphere
- (iii) Presence of impurity in the iron.

Various theories have been proposed to explain the phenomenon of rusting of iron but the accepted theory is the

modern electrochemical theory. When impure iron comes in contact with water containing dissolved carbon dioxide, a voltaic cell is set up. The iron and other impurities act as electrodes while water having dissolved oxygen and carbon dioxide acts as an electrolyte. Iron atoms pass into solution as ferrous ions.

$$Fe \longrightarrow Fe^{2+} + 2e$$

Iron, thus, acts as anode.

The impurities act as cathode. At the cathode, the electrons are used in forming hydroxyl ions.

$$H_2O + O + 2e \longrightarrow 2OH^-$$

In presence of dissolved oxygen, ferrous ions are oxidised to ferric ions which combine with hydroxyl ions to form ferric hydroxide.

$$Fe^{3+} + 3OH^{-} \longrightarrow Fe(OH)_{3}$$
Rust

$$[2Fe^{2+} + H_2O + O \longrightarrow 2Fe^{3+} + 2OH^-]$$

Corrosion or rusting is a surface phenomenon and thus, the protection of the surface prevents the corrosion. Iron can be protected from the rusting by use of following methods:

- (i) Applying paints, lacquers and enamels on the surface of iron.
- (ii) By forming a firm and coherent protective coating of ferrosoferric oxide. This is done by passing steam over hot iron.
- (iii) By coating a thin film of zinc, tin, nickel, chromium, aluminium, etc.

# 14.14 POSITION OF COINAGE METALS IN PERIODIC TABLE

Group		vin		1B	mB
Period	(8)	(9)	(10)	(11)	(12)
4	Fe 26	Co 27	Ni 28	Cu 29	Zn 30
5	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48
6	Os 76	Ir 77	Pt 78	Au 79	Hg 80

IB subgroup (group 11) of the periodic table consists of four metals—copper (Cu), silver (Ag), gold (Au) and unununium (Uuu)\*. These are collectively called as copper metals (copper being the predominant member) or coinage metals or currency metals because these (Cu, Ag and Au) have been used in the past in making coins for currency. These are d-block elements as the differentiating electron is accommodated on (n-1)d energy shell. Copper is a member of 3d series, silver is a member of 4d series, Au is a member of 5d series and Uuu is a member of 6d series. They show relationship with Ni, Pd and Pt (group VIII) which are their left hand neighbours and also with Zn, Cd and Hg (group IIB) which are their right hand neighbours in the periodic table. Thus, these occupy position

between VIII and IIB groups of the periodic table. Their inclusion in the same subgroup is justified on the basis of:

- (a) same electronic configuration and
- (b) similar characteristics or gradation in the properties.
- 1. Electronic configuration: They have similar electronic configuration. The distribution of the electrons in various energy shells of these atoms is shown below:

Cu 29 2, 8, 18, 1 
$$1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^1$$
  
Ag 47 2, 8, 18, 18, 1  $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^64d^{10}, 5s^1$   
Au 79 2, 8, 18, 32, 18, 1  $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^64d^{10}4f^{14}, 5s^25p^65d^{10}, 6s^1$   
Uuu 111 2, 8, 18, 32, 32, 18, 1  $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^64d^{10}4f^{14}, 5s^25p^65d^{10}5f^{14}, 6s^26p^66d^{10}, 7s^1$ 

The electronic configuration shows that the outermost shell of these elements has one electron  $(ns^1)$  while the penultimate shell contains 18 electrons  $[(n-1)s^2p^6d^{10}]$ , i.e., general configuration  $(n-1)s^2(n-1)p^6(n-1)d^{10}ns^1$ . However, (n-1)d shell has not attained stability and one or more electrons sometimes jump to the outermost shell thereby increasing the valency electrons. As a result, the atoms or ions take up the new configuration.

It is for this reason that these elements are considered as the end members of transition series. In higher valency states these elements, therefore, show properties similar to those of the corresponding transition elements of VIII group.

**2. Valency:** Being transition elements, these show variable valency. Copper forms both cuprous (Cu<sup>+</sup>) and cupric (Cu<sup>2+</sup>) ions. The cuprous ions, however, have a tendency to change into cupric and thus, soluble cuprous salts are not stable.

$$2Cu^{+} \longrightarrow Cu^{2+} + Cu$$

The insoluble cuprous salts as  $Cu_2Cl_2$ ,  $Cu_2I_2$ ,  $Cu_2(CN)_2$ ,  $Cu_2(CNS)_2$  are stable.

Silver shows mainly monovalency. The compounds of divalent silver are rare.

Gold like copper also forms two series of salts showing monovalency (aurous salts, Au<sup>+</sup>) and trivalency (auric salts, Au<sup>3+</sup>). The aurous salts are not stable and change into auric salts.

$$3Au^+ \longrightarrow Au^{3+} + 2Au$$
encies are: Copper: Divalence

Thus, stable valencies are: Copper; Divalency

Silver; Monovalency Gold; Trivalency

<sup>\*</sup>Uuu is a synthetic and radioactive element. It is unstable and not much is known about its properties.

**3. Physical Properties:** (a) These are tough, ductile and highly malleable metals. Silver and gold are more ductile and malleable than copper. (b) They are good conductors of heat and electricity. Silver is the best conductor. (c) They have high melting and boiling points. The availability of inner d electrons enhances the bonding between atoms in the metal crystal and results in the greater hardness and higher melting points of these elements like other transition elements.

Metal	Cu	Ag	Au
M.Pt. (°C)	1083	961	1063
B.Pt. (°C)	2595	2180	2700

(d) Atomic size: The atomic size are relatively small. Gold and silver have nearly the same atomic size. (This is due to lanthanide contraction associated with the filling of the 4f shell). The atomic volumes are also small and both silver and gold have the same values.

Metal	Cu	Ag	Au
Atomic radii Å	1.17	1.34	1.34
Atomic volume	7.1	10.3	10.2

**(e) Density:** These are heavy metals. Density increases gradually as the atomic number increases.

Metal	Cu	Ag	Au
Density	8.96	10.5	19.3

**(f) Ionisation Energy:** Because of the smaller atomic size and increased nuclear charge, their ionisation energies are high. The ionisation energies do not show the expected trend with increasing atomic number; the values decrease from copper to silver but increase in going to gold.

Metal	Cu	Ag	Au
I.E. (eV)	7.72	7.57	9.2

The unexpected behaviour from Ag to Au is due to the fact that the atomic size of Ag and Au are the same while atomic charge increases from 47 to 79.

**(g) Oxidation potentials:** The standard oxidation potentials of coinage metals are negative.

$$Cu \longrightarrow Cu^{2+} + 2e \qquad E_{ox}^{\circ} = -0.34 \text{ volt}$$

$$Ag \longrightarrow Ag^{+} + e \qquad E_{ox}^{\circ} = -0.80 \text{ volt}$$

$$Au \longrightarrow Au^{3+} + 3e \qquad E_{ox}^{\circ} = -1.42 \text{ volt}$$

$$Cu \longrightarrow Cu^{+} + e \qquad E_{ox}^{\circ} = -0.52 \text{ volt}$$

$$Au \longrightarrow Au^{+} + e \qquad E_{ox}^{\circ} = -1.70 \text{ volt}$$

The values suggest that the atoms of coinage metals have little tendency to lose electron or electrons. Thus, these elements are feebly electropositive. The nobility increases in the order  $Cu \longrightarrow Ag \longrightarrow Au$ . Because of nobility, they are frequently found in their native state (silver and gold almost exclusively).

(h) Colour of the salts: The monovalents salts are colourless as they have  $(n-1)d^{10}$  configuration.

Cu<sup>+</sup> 2, 8, 18 (3
$$d^{10}$$
)  
Ag<sup>+</sup> 2, 8, 18, 18 (4 $d^{10}$ )  
Au<sup>+</sup> 2, 8, 18, 32, 18 (5 $d^{10}$ )

The salts in higher oxidation states are coloured as unpaired orbital or orbitals are present in (n-1)d energy shell.

$$Cu^{2+}$$
 2, 8, 17 (one 3*d* orbital singly occupied)  
 $Ag^{2+}$  2, 8, 18, 17 (one 4*d* orbital singly occupied)  
 $Au^{3+}$  2, 8, 18, 32, 16 (two 5*d* orbitals singly occupied)

Cu (II) salts are generally bluish or green, and Au (III) salts are yellow.

- (i) Magnetic nature: Cu (I), Ag (I) and Au (I) ions are diamagnetic as all the orbitals are fully paired while Cu (II), Ag (II) and Au (III) ions are paramagnetic as one or two orbitals are singly occupied.
- **4. Chemical Properties:** The chemical activity of a metal depends on the three hypothetical stages, each one involving an energy change.

$$\begin{array}{c} \text{Metal} \xrightarrow{\text{(Sublimation energy)}} & \text{Gaseous atoms} \xrightarrow{\text{(Ionisation potential)}} & \text{Ions} \\ & \xrightarrow{\text{(Hydration energy)}} & \text{Hydrated ions} \end{array}$$

A high heat of sublimation and high ionisation potential will reduce the tendency of the metal to react. In the case of coinage metals both sublimation energy and ionisation potential have very high values and thus, coinage metals are less reactive. The chemical activity decreases from Cu to Au.

- (a) Action of air: Gold and silver are not affected by air but copper on long exposure becomes converted with a greyish green film of basic carbonate, CuCO<sub>3</sub>Cu(OH)<sub>2</sub>.
- **(b) Affinity for oxygen:** Their affinity for oxygen decreases from copper to gold. Only copper combines with oxygen on heating. Copper oxide when strongly heated is reduced to cuprous oxide, silver oxide breaks up into silver and oxygen at about 300°C whereas gold oxide breaks up at 250°C. Cu<sub>2</sub>O difficult to break.

$$2Ag_2O \xrightarrow{300^{\circ}C} 4Ag + O_2$$

$$2Au_2O \xrightarrow{250^{\circ}C} 4Au + O_2$$

(c) Action of water: The coinage metals are not affected by water or steam. However, copper is attacked by steam at red hot state.

Cu (red hot) + 
$$H_2O \longrightarrow CuO + H_2$$

- (d) Action of sulphur: Both copper and silver combine directly with sulphur. Both copper and silver are found in the nature in the form of sulphides.
- (e) Action of halogens: Coinage metals react much more readily with the free halogens than with any other element. Copper combines with halogens at ordinary temperatures.

$$Cu + X_2 \longrightarrow CuX_2$$

Silver reacts slowly while, gold reacts with dry halogens on heating.

$$2Au + 3X_2 \longrightarrow 2AuX_3$$

(f) Action of acids: Copper, silver and gold do not liberate hydrogen from dilute acids as they are present below hydrogen in the electrochemical series. Copper dissolves in het dilute acids HCl or H<sub>2</sub>SO<sub>4</sub> only in presence of air or oxygen.

$$Cu + 2HCl + \frac{1}{2}O_2 \longrightarrow CuCl_2 + H_2O$$

$$Cu + H_2SO_4 + \frac{1}{2}O_2 \longrightarrow CuSO_4 + H_2O$$
(dil.)

Copper and silver dissolve readily in acids which act as oxidising agents, e.g., dil. and conc. HNO<sub>3</sub>, conc. H<sub>2</sub>SO<sub>4</sub>.

$$\begin{array}{c} H_2SO_4(\text{conc.}) \longrightarrow H_2O + SO_2 + O \\ \hline Cu + H_2SO_4 + O \longrightarrow CuSO_4 + H_2O \\ \hline \hline Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O \\ \hline H_2SO_4(\text{conc.}) \longrightarrow H_2O + SO_2 + O \\ \hline 2Ag + H_2SO_4 + O \longrightarrow Ag_2SO_4 + H_2O \\ \hline \hline 2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + SO_2 + 2H_2O \\ \hline 2HNO_3(\text{conc.}) \longrightarrow H_2O + 2NO_2 + O \\ \hline Cu + 2HNO_3 + O \longrightarrow Cu(NO_3)_2 + H_2O \\ \hline \hline Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O \\ \hline 2HNO_3(\text{conc.}) \longrightarrow H_2O + 2NO_2 + O \\ \hline 2Ag + 2HNO_3 + O \longrightarrow 2AgNO_3 + H_2O \\ \hline \hline 2Ag + 4HNO_3 \longrightarrow 2AgNO_3 + 2NO_2 + 2H_2O \\ \hline 2HNO_3(\text{dil.}) \longrightarrow H_2O + 2NO + 3[O] \\ \hline [Cu + 2HNO_3 + O \longrightarrow Cu(NO_3)_2 + H_2O] \times 3 \\ \hline \hline 3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O \\ \hline 2HNO_3(\text{dil.}) \longrightarrow H_2O + 2NO + 3[O] \\ \hline [2Ag + 2HNO_3 + O \longrightarrow 2AgNO_3 + H_2O] \times 3 \\ \hline \hline 6Ag + 8HNO_3 \longrightarrow 6AgNO_3 + 2NO + 4H_2O \\ \hline 3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO + 2H_2O \\ \hline Gold only dissolves in aqua-regia. \\ \hline [HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2Cl] \times 3 \\ \hline (conc.) & (conc.) \\ \hline (conc.) & HAUCl_4 \times 2 \\ \hline (conc.) & HAUCl_4 \times 2 \\ \hline (Au + 3Cl \longrightarrow AuCl_3] \times 2 \\ \hline (Au + 3HNO_3 + 1HCl \longrightarrow HAuCl_4 \times 3NOCl + 6H_2O \\ \hline Or & HNO_3 + 3HCl \longrightarrow NO + 2H_2O + 3Cl \\ \hline Au + HCl + 3Cl \longrightarrow HAuCl_4 \\ \hline Au + HNO_3 + 4HCl \longrightarrow HAuCl_4 + NO + 2H_2O \\ \hline \end{array}$$

or

or

- (g) Alloy formation: Copper, silver and gold readily form alloys with each other and with many other metals. They form amalgams with mercury.
- (h) Complex formation: These metals have strong tendency to form complex compounds. A variety of anionic and cationic complexes are formed. The principal coordination numbers are 2 or 4. Some complex compounds are listed below:

$K_3[Cu(CN)_4]$	$K[Ag(CN)_2]$	$K[Au(CN)_2]$
Pot. cuprocyanide	Pot argentocyanide	Pot. aurocyanide
$[Cu(NH_3)_4]SO_4$	Ag(NH <sub>3</sub> ) <sub>2</sub> Cl	K[AuCl <sub>4</sub> ]
Cuprammonium	Silver ammonium	Pot. auric chloride
sulphate	chloride	•

#### 5. Nature of Compounds

(a) Oxides: The monoxides of the type M<sub>2</sub>O are weakly basic. The basicity does not vary regularly in the group, Ag<sub>2</sub>O being most basic. These are insoluble in water. CuO shows basic nature while Au<sub>2</sub>O<sub>3</sub> shows acidic nature as it dissolves in strong alkalies.

$$\begin{array}{c} CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \\ Au_2O_3 + 2NaOH \longrightarrow 2NaAuO_2 + H_2O \\ \hline Sodium aurate \end{array}$$

The oxides of silver and gold are thermally unstable. These can be easily reduced with reducing agents. The hydroxides are weak bases. The hydroxides of Ag and Au are unstable.

(b) Halides: Halides of Cu<sup>+</sup>, Ag<sup>+</sup> and Au<sup>+</sup> are insoluble in water except AgF. The halides of silver get decomposed in light. AgCl is soluble in ammonia solution. AgBr is partially soluble while AgI is insoluble.

$$AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O$$
Soluble

- (c) Sulphides: Cu, Ag and Au form sulphides, Cu<sub>2</sub>S, CuS; Ag<sub>2</sub>S; Au<sub>2</sub>S and Au<sub>2</sub>S<sub>3</sub>. Copper and silver sulphides are insoluble in ammonium sulphide but gold sulphides dissolve forming thioaurates.
- (d) Oxysalts: Copper forms stable oxysalts in divalent state while silver stable oxysalts are known in monovalent state. Gold does not form oxysalts. The oxysalts of copper and silver decomposes on heating.

$$CuCO_{3} \longrightarrow CuO + CO_{2}$$

$$Ag_{2}CO_{3} \longrightarrow 2Ag + CO_{2} + \frac{1}{2}O_{2}$$

$$Cu(NO_{3})_{2} \longrightarrow CuO + 2NO_{2} + \frac{1}{2}O_{2}$$

$$AgNO_{3} \longrightarrow Ag + NO_{2} + \frac{1}{2}O_{2}$$

$$CuSO_{4} \longrightarrow CuO + SO_{2} + \frac{1}{2}O_{2}$$

$$Ag_{2}SO_{4} \longrightarrow 2Ag + SO_{2} + O_{2}$$

## Similarities of Copper with Nickel and Zinc

## (1) Similarities with Nickel

- (i) Both are transition metals. These are hard, malleable and ductile. They have high melting and boiling points. They are good conductors of heat and electricity.
- (ii) Both the metals show variable valency. The stable valency is the divalency. Both form two series of salts: cuprous and cupric; nickelous and nickelic. Stable salts are cupric and nickelous (divalency). The salts are coloured—cupric salts are bluish and green while nickelous salts are green.
  - (iii) Their  $M^{2+}$  ions are similar in size.

$$Cu^{2+} = 0.69\text{Å} \text{ Ni}^{2+} = 0.72\text{Å}$$

- (iv) Both form black sulphides, CuS and NiS.
- (v) Both are acted upon by oxidising acids.
- (vi) Both form similar sulphates.

Both are soluble in water and form double sulphates of the type,  $(NH_4)_2SO_4\cdot MSO_4\cdot 6H_2O$ .

(vii) The oxides of both can be obtained by heating their carbonates or nitrates.

$$\begin{aligned} &\text{NiCO}_{3} \longrightarrow \text{NiO} + \text{CO}_{2} \\ &\text{CuCO}_{3} \longrightarrow \text{CuO} + \text{CO}_{2} \\ &\text{Ni(NO}_{3})_{2} \longrightarrow \text{NiO} + 2\text{NO}_{2} + \frac{1}{2}\text{O}_{2} \\ &\text{Cu(NO}_{3})_{2} \longrightarrow \text{CuO} + 2\text{NO}_{2} + \frac{1}{2}\text{O}_{2} \end{aligned}$$

CuO and NiO are basic in nature. These can be reduced with hydrogen.

- (viii) Basic carbonates of the general formula  $MCO_3 \cdot M(OH)_2$  are precipitated on treating their salts with sodium carbonate. Normal carbonates are obtained by using sodium bicarbonate.
- (ix) Both have a tendency to form complexes. They usually show coordination number 4.

- (x) Both of them show catalytic properties.
- (xi) Both form a number of alloys.

# (2) Similarities with Zinc

- (i) Both are metals.
- (ii) Both show divalency.
- (iii) Both form oxides of the type MO, i.e., CuO and ZnO. These can be obtained by heating their carbonates or nitrates.

$$ZnCO_3 \longrightarrow ZnO + CO_2$$
  
 $Zn(NO_3)_2 \longrightarrow ZnO + 2NO_2 + \frac{1}{2}O_2$ 

(iv) Both form similar compounds. Sulphides, phosphates and carbonates are insoluble in water while chlorides and sulphates are soluble in  $H_2O$ .

- (v) Both form hydrated sulphates,  $CuSO_4.5H_2O$  and  $ZnSO_4.7H_2O$ . They also form double sulphates of the type,  $(NH_4)_2SO_4.MSO_4.6H_2O$ .
  - (vi) Hydrated chlorides cannot be dehydrated by heating.

$$ZnCl_2 \cdot 2H_2O \longrightarrow Zn(OH)Cl + HCl + H_2O$$

(vii) Both have a tendency to form complexes.

 $\begin{aligned} & [Cu(NH_3)_4]SO_4 & & [Zn(NH_3)_4]SO_4 \\ & K_3[Cu(CN)_4] & & K_2[Zn(CN)_4] \end{aligned}$ 

- (viii) Both form a number of alloys.
- (ix) Basic carbonates of the general formula  $MCO_3 \cdot M(OH)_2$  are precipitated on treating their salts with sodium carbonate. Normal carbonates are obtained by using sodium bicarbonate.

# 14.15 COPPER

Copper has been known to mankind from prehistoric times. It was alloyed with other metals and the use of bronze in Egypt is reported as early as 350 B.C. Romans and Greeks obtained this metal from the island of Cyprus from which the name 'cuprum' was derived.

**Occurrence:** Copper constitutes only 0.0001 per cent of the earth's crust. Its deposits, however, are concentrated. Copper is found in nature in the following forms.

- 1. Native state: Copper is found in the metallic condition in large quantities near lake Superior in U.S.A.; in the Ural mountains (Russia) and Sweden.
- **2.** Combined state: The principal ores of copper are sulphides, oxides and basic carbonates.

## ■ Sulphide Ores

- (i) Chalcopyrites or copper pyrites, CuFeS<sub>2</sub>
- (ii) Chalcocite or copper glance, Cu<sub>2</sub>S
- (iii) Bornite, Cu<sub>3</sub>FeS<sub>3</sub>

#### Oxide Ore

Cuprite (red), Cu<sub>2</sub>O

#### ■ Basic Carbonates

- (i) Malachite (green), CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>
- (ii) Azurite (blue), 2CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>

Copper is found to a very minute extent in the animal body where it is said to catalyse the action of iron in the formation of haemoglobin. It is present in traces in the cereals and potatoes. It occurs as a red colouring matter of the feathers of certain birds. Milk has a very low copper content.

India is not rich in copper ores. Copper is found in India mainly in Singhbhum district (Jharkhand), Matigara and Dharwar. The copper belt in Rajasthan (Khetri) is at present under extensive development.

#### Extraction

Copper may be extracted by different methods depending upon the nature of the ore and the % of copper. The methods may be divided into two categories.

#### 1. From sulphide ores:

- (a) Dry process or smelting process: This is applied to those ores in which copper content is more than 3%.
- (b) Wet process or hydro-metallurgical process: This is applied to poor ores containing small percentage of copper.
  - 2. From non-sulphide ores: Leaching process.

**Dry process for the extraction of copper:** Copper is extracted mainly from copper pyrites by dry process or smelting process. The process of extraction of copper from copper pyrites involves the following steps:

(i) Concentration of the ore: The concentration of the sulphide ores is done by froth floatation process. The ores are powdered and sieved and then thrown into tanks of water to which pine oil and potassium xanthate have been added. A strong stream of air is passed which agitates the whole mass. Froth is produced which carries along the particles of the ore

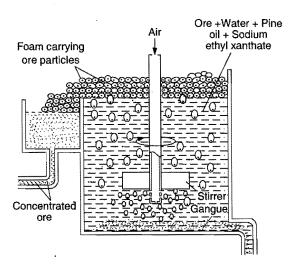


Fig. 14.8

to the surface of the liquid while the impurities settle to the bottom of the tank (Fig. 14.8). The froth is continuously separated. This is the concentrated ore.

- (ii) Roasting: The concentrated ore is heated strongly in a current of air on the hearth of the reverberatory furnace (Fig. 14.9). During roasting the following changes take place.
  - (a) Free sulphur is oxidised and removed as sulphur dioxide.

$$S + O_2 \longrightarrow SO_2$$

(b) The arsenic and antimony present in the ore are removed as volatile oxides.

$$4As + 3O_2 \longrightarrow 2As_2O_3$$

$$4Sb + 3O_2 \longrightarrow 2Sb_2O_3$$

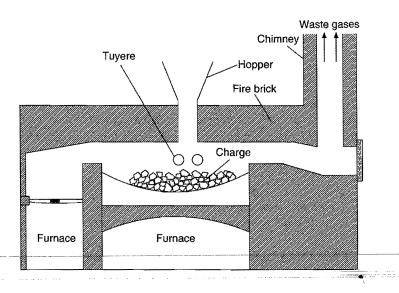


Fig. 14.9

(c) The pyrite is converted into cuprous sulphide and ferrous sulphide with evolution of sulphur dioxide.

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

(d) The sulphides of copper and iron are partially oxidised.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$
  
 $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$ 

(iii) **Smelting:** The roasted ore is mixed with coke and silica and transferred to a small blast furnace (Fig. 14.10). The

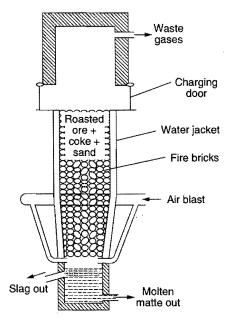


Fig. 14.10

mixture is heated in the presence of excess of air. The modern blast furnace is made of steel lined inside with refractory bricks and is about 15 to 20 feet in height. It is water jacketed throughout and is provided near the top with a waste gas outlet.

The air blast enters the furnace through tuyeres. The following changes occur in the blast furnace.

(a) The cuprous oxide reacts with ferrous sulphide.

$$FeS + Cu_2O \longrightarrow FeO + Cu_2S$$

[Iron has greater affinity for oxygen than copper. The copper oxide formed reacts with unchanged iron sulphide to form iron oxide and reproduce copper sulphide. So it is difficult to oxidise cuprous sulphide until whole of the iron sulphide is oxidised].

- (b) Most of the iron sulphide is oxidised to ferrous oxide.  $2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2$
- (c) Ferrous oxide combines with silica and forms ferrous silicate. By this reaction most of the iron is removed as slag.

$$\frac{\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3}{\text{Ferrous silicate}}$$

The lowest point of the furnace consists of a shallow hearth in which the molten mass collects which is known as 'Matte'. The matte contains mostly cuprous sulphide with a little iron sulphide.

**(iv)** Bessemerisation: The matte obtained from smelting is transferred to a Bessemer converter. Some sand (silica) is added and a blast of air is blown through the molten mass. The Bessemer converter is usually a pear shaped steel vessel lined with magnesite and quartz. It is fitted with air-blast tuyeres and mounted in such a way that it can be tilted in the desired direction (Fig. 14.11).

The following reactions occur in the Bessemer converter.

(a) Remaining ferrous sulphide gets oxidised.

 $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$ 

Fig. 14.11

Molten matte + Sand

(b) Ferrous oxide combines with silica to form slag which is drained out at intervals by tilting the vessel. In about three hours time, all the iron is removed as ferrous silicate.

$$FeO + SiO_2 \longrightarrow FeSiO_3$$
(Slag)

(c) The blast of air is continued for almost another two hours. Excess of silica is absorbed by basic lining of the con-

verter and part of cuprous sulphide is oxidised which combines with remaining cuprous sulphide to form free copper metal.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
  
 $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$ 

This presents an example of auto-reduction.

The molten copper is poured off and allowed to cool. During cooling, the dissolved sulphur dioxide comes out and large blisters are formed on the surface. Hence, the metal formed is given the name 'blister copper'. Blister copper consists 98% copper and 2% impurities.

- (v) Refining: Blister copper is subjected to refining by either of the following two methods.
- (a) Refining by poling: The impure metal is melted in a reverberatory furnace lined with silica. A part of copper metal is oxidised to cuprous oxide which dissolves in the melt and supplies oxygen to the more basic elements contained in it as impurity. These oxides either volatilise or combine with silica forming slag. The oxide of copper which remains in the mass is reduced by introducing poles of green wood. The gas (hydrocarbons) bubbles originating from the wood act as reducing agents. The mass is stirred vigorously with these poles. The process is thus called poling.

This process produces copper of about 99.5% purity and is known as tough pitch copper.

**(b) Electrolytic refining:** Copper is usually refined electrolytically. The electrolytic bath consists about 15% copper sulphate solution having 5% sulphuric acid. The anodes are of blister copper and cathodes are thin sheets of pure copper (Fig. 14.12).

As the current flows, copper from anodes dissolves while pure copper is deposited on the cathodes.

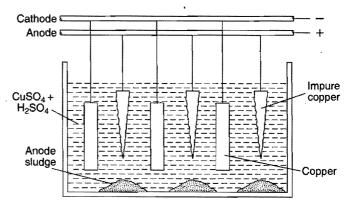


Fig. 14.12

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$
Cathode
$$Cu^{2+} + 2e \longrightarrow Cu$$

$$Cu + SO_4^{2-} \longrightarrow CuSO_4 + 2e$$

The more electropositive impurities like Fe, Zn, Ni, Co, etc., dissolve in the solution and less electropositive

impurities such as Ag, Au and Pt collect below the anode in the form of anodic mud. Electrolytic copper has a purity of 99.96–99.99%.

Wet process or Hydrometallurgical process: The essential principle of this process consists in the conversion of copper present in the ore into soluble copper compound and precipitation of copper by addition of iron or by electrolytic process.

Big heaps of copper sulphide ores are exposed to air and rain. Water is also sprayed at times, if necessary. After a year's time, the copper sulphide is slowly oxidised to copper sulphate. The liquor which flows from the bottom of the heaps is run into pans. Copper is precipitated from the liquor by the addition of scrap iron. The precipitate is dried, melted and refined.

$$2Cu_2S + 5O_2 \longrightarrow 2CuSO_4 + 2CuO$$
  
 $CuSO_4 + Fe \longrightarrow Cu + FeSO_4$   
(ppt.)

**2.** Extraction of copper from non-sulphide ores: The oxide and carbonate ores are crushed and concentrated by gravity process. The concentrated ores are calcined in reverberatory furnace. The carbonate decomposes to form the oxide and the impurities either volatilise or are oxidised.

$$CuCO_3 \cdot Cu(OH)_2 \longrightarrow 2CuO + CO_2 + H_2O$$

The oxide so formed is either reduced with carbon in reverberatory furnace or leached with dilute H<sub>2</sub>SO<sub>4</sub>.

$$\begin{array}{c} \text{CuO} + \text{C} & \longrightarrow \text{Cu} + \text{CO} \\ \text{Cu}_2\text{O} + \text{C} & \longrightarrow 2\text{Cu} + \text{CO} \\ \text{CuO} + \text{H}_2\text{SO}_4 & \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O} \end{array}$$

FLOW SHEET FOR THE EXTRACTION OF COPPER Copper pyrites (CuFeS<sub>2</sub>) Crushed and sieved Concentration by froth floatation Powdered ore + water + pine oil + air - sulphide ore in the froth Roasting in reverberatory furnace in presence of air  $\begin{array}{c} S + O_2 \longrightarrow SO_2 \\ 4As + 3O_2 \longrightarrow 2As_2O_3 \end{array}$  $2\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2$ Silica + coke ----- Roasted ore Smelting in blast furnace in presence of air  $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$  $FeO + SiO_2 \longrightarrow FeSiO_3$  (Slag)  $\xrightarrow{\text{Silica}}$  Matte (Cu<sub>2</sub>S, FeS) Bessemerisation in bessemer converter in presence of air  $\begin{array}{l} {\rm 2FeS} \, + \, {\rm 3O_2} \longrightarrow {\rm 2FeO} \, + \, {\rm 2SO_2} \\ {\rm FeO} \, + \, {\rm SiO_2} \longrightarrow {\rm FeSiO_3} \, \, ({\rm Slag}) \\ \end{array}$  $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$  $2Cu_2O + Cu_2S \xrightarrow{Auto} 6Cu + SO_2$ 

Blister copper (98% Cu + 2% impurities)

Electrolytic refining
Anode–Impure copper plates
Cathode–Pure copper plates
Electrolyte–CuSO<sub>4</sub> soln. + H<sub>2</sub>SO<sub>4</sub>
Pure copper deposited at cathode

Pure copper (99.6–99.9%)

Copper sulphate solution obtained is then electrolysed using copper sheet as cathode and lead plate as anode. Copper can also be recovered by using scrap iron.

$$CuSO_4 + Fe \longrightarrow Cu + FeSO_4$$

### Properties

Physical: (a) It is a reddish coloured lustrous metal.

- (b) It is highly malleable and ductile.
- (c) It has specific gravity 8.9.
- (d) It has high melting and boiling points (m.pt. 1083°C, b.pt. 2580°C).
- (e) It is good conductor of heat and electricity (next to silver).
- (f) Its atomic radii is 1.17Å and ionisation potential is 7.72 eV.
- (g) Molten copper absorbs sulphur dioxide which it gives out on cooling.

**Chemical:** Copper is chemically less reactive as it has high heat of sublimation and high ionisation potential.

(a) Action of air and oxygen: Copper is not affected by dry air at ordinary temperatures but when exposed to air and moisture, it is covered by a green thin film which was formerly supposed to be the basic carbonate but consists of *bronchantite*, CuSO<sub>4</sub>·3Cu(OH)<sub>2</sub> or *atacamite*, CuCl<sub>2</sub>·3Cu(OH)<sub>2</sub> due to presence of SO<sub>2</sub> and HCl in the atmosphere.

$$8Cu + 6H2O + 2SO2 + 5O2 \longrightarrow 2[CuSO4·3Cu(OH)2]$$

$$2Cu + H2O + CO2 + O2 \longrightarrow CuCO3·Cu(OH)2$$
Basic carbonate

The layer protects the rest of the metal from further action. When heated in oxygen, it first forms red cuprous oxide (Cu<sub>2</sub>O) which changes into black cupric oxide (CuO). If the temperature is raised above 1100°C, cupric oxide changes back to cuprous oxide.

$$4Cu + O_2 \longrightarrow 2Cu_2O \text{ (red)}$$

$$2Cu_2O + O_2 \longrightarrow 4CuO \text{ (black)}$$

$$2CuO \xrightarrow{1100^{\circ}C} Cu_2O + \frac{1}{2}O_2$$

**(b)** Action of water: Water at ordinary temperature has no action on copper. However, when steam is passed over red hot copper, hydrogen is evolved.

$$Cu + H_2O \xrightarrow{\text{Red heat}} CuO + H_2$$

(c) Action of acids: Non-oxidising acids (HCl and dil.  $H_2SO_4$ ) do not have any effect on copper. However, they dissolve the metal in presence of air.

2Cu + 4HCl (dil. or conc.) + 
$$O_2 \longrightarrow 2CuCl_2 + 2H_2O$$
  
2Cu +  $2H_2SO_4$  (dil.) +  $O_2 \longrightarrow 2CuSO_4 + 2H_2O$ 

Copper is readily affected by oxidising acids (conc.  $H_2SO_4$ , dilute and conc.  $HNO_3$ .)

Conc.  $H_2SO_4$ :  $SO_2$  is evolved on heating.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + O$$

$$Cu + O + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

**Dilute HNO<sub>3</sub>:** NO is evolved on heating.  

$$2HNO_3 \longrightarrow H_2O + 2NO + 3[O]$$

$$[Cu + 2HNO_3 + O \longrightarrow Cu(NO_3)_2 + H_2O] \times 3$$

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Conc. HNO<sub>3</sub>: NO<sub>2</sub> is evolved on heating.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

$$Cu + 2HNO_3 + O \longrightarrow Cu(NO_3)_2 + H_2O$$

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Copper metal reacts with hydrobromic acid (HBr) and hydroiodic acid forming complexes.

$$2Cu + 2HBr \longrightarrow 2CuBr + H_2$$
  
 $2CuBr + 2HBr \longrightarrow H_2[Cu_2Br_4]$ 

Copper plates are slowly attacked by acetic acid (vinegar) in presence of air to form basic copper acetate (verdigris).

**(d) Action of ammonia:** Copper is dissolved by aqueous ammonia in the presence of air or oxygen with the formation of a complex.

$$2Cu + 8NH_3 + 2H_2O + O_2 \longrightarrow 2[Cu(NH_3)_4](OH)_2$$

However, when ammonia gas is passed over red hot copper, the nitrogen is absorbed by the metal leaving hydrogen free.

**(e) Action of halogens :** Copper combines with halogens directly.

$$Cu + Cl_2 \xrightarrow{Heat} CuCl_2$$

$$Cu + Br_2 \xrightarrow{Heat} CuBr_2$$

$$Cu \, + \, I_2 \, \xrightarrow{Heat} \, Cu I_2$$

Moist chlorine rapidly attacks copper even at ordinary temperatures.

(f) As a reducing agent: Copper reduces oxides of nitrogen to elementary nitrogen and ferric ion to ferrous ion.

$$2Cu + 2NO \longrightarrow 2CuO + N_2$$

$$2Fe^{3+} + Cu \longrightarrow 2Fe^{2+} + Cu^{2+}$$

The etching of designs on copper plates using ferric chloride is based on this property.

$$2FeCl_3 + Cu \longrightarrow CuCl_2 + 2FeCl_2$$

(g) Displacement reactions: Copper displaces Ag, Au and platinum metals from their salt solutions.

$$2AgNO_3 + Cu \longrightarrow 2Ag + Cu(NO_3)_2$$
  
 $3Cu + 2AuCl_3 \longrightarrow 3CuCl_2 + 2Au$ 

#### Uses

Copper is most useful metal (only next to iron) on account of its properties as it is stable in air and water and good conductor of heat and electricity.

It is used,

- (i) in the manufacture of electrical wires, cables, etc.
- (ii) for making vacuum pans, heating utensils, calorimeters, etc.
  - (iii) for electroplating and electrotyping.
  - (iv) for making coins, ornaments and jewellery.
- (v) for making various compounds which are used as insecticides, pesticides and pigments.
- (vi) for making a large number of alloys. The important alloys are listed below:

Alloy	Composition	Uses
(a) Brass	Cu 60–80%, Zn 40–20%	Domestic utensils, condensers, cartridges
(b) Bronze	Cu 75–90%, Sn 25–10%	cases, etc. Coins, statues, utensils, machine parts, bells, etc.
(c) German silver	Cu 56%, Zn 24%, Ni 20%	Utensils, ornaments, resistance coils.
(d) Gun metal	Cu 87%, Sn 10%, Zn 3%	Machine parts, guns.
(e) Rolled gold	Cu 95%, Al 5%	Artificial jewellery.
(f) Constantan	Cu 60%, Ni 40%	Electrical resistances.
(g) Monel metal	Cu 30%, Ni 67%, Fe 3%	Chemical plants, automobile engine parts.
(h) Phosphorus bronze	Cu 85%, Sn 13%, P 2%	Gears, aerials, propellers, etc.

# 14.16 COMPOUNDS OF COPPER

## Copper Forms two Series of Compounds

1. Cuprous compounds: In which copper is monovalent. Most of the cuprous compounds are colourless and diamagnetic as 3d-shell is completely filled.  $Cu_2O$  and  $Cu_2S$  are red and black, respectively, which are exceptions. Cuprous compounds are generally insoluble in water. The soluble compounds are unstable in aqueous solutions, since they disproportionate to  $Cu^{2+}$  and Cu.

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

Cuprous compounds can be obtained by passing sulphur dioxide through a solution containing copper sulphate and sodium salt. Some examples are given below:

(i) 
$$2\text{CuSO}_4 + 2\text{NaCl} + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \\ 2\text{CuCl} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4 \\ \text{Cuprous chloride}$$

(ii) 
$$2\text{CuSO}_4 + 2\text{NaBr} + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \\ 2\text{CuBr} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4 \\ \text{Cuprous bromide}$$

(iii) 
$$2\text{CuSO}_4 + 2\text{NaI} + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \\ 2\text{CuI} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4 \\ \text{Cuprous iodide}$$

(iv) 
$$2\text{CuSO}_4 + 2\text{NaCN} + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \\ 2\text{CuCN} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4 \\ \text{Cuprous cyanide}$$

(v) 
$$2\text{CuSO}_4 + 2\text{NaCNS} + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \\ 2\text{CuCNS} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4 \\ \text{Cuprous thiocyanate}$$

The reactions (iii) and (iv) can take place even in absence of sulphur dioxide.

$$2\text{CuSO}_4 + 4\text{NaI} \longrightarrow 2\text{CuI} + 2\text{Na}_2\text{SO}_4 + \text{I}_2$$
  
 $2\text{CuSO}_4 + 4\text{NaCN} \longrightarrow 2\text{CuCN} + 2\text{Na}_2\text{SO}_4 + (\text{CN})_2$ 

The true molecular formula of cuprous compounds is still doubtful. There are experimental evidences for dimeric molecule.

## Cuprous Chloride, Cu<sub>2</sub>Cl<sub>2</sub>

## **■** Preparation

It is prepared—

(i) by heating excess of copper with concentrated hydrochloric acid in presence of a little potassium chlorate.

$$\begin{aligned} Cu + 2HCl + O &\longrightarrow CuCl_2 + H_2O \\ CuCl_2 + Cu &\longrightarrow Cu_2Cl_2 \end{aligned}$$

(ii) by boiling copper sulphate solution with excess of copper turnings in presence of hydrochloric acid.

$$\begin{aligned} \text{CuSO}_4 + 2\text{HCl} &\longrightarrow \text{CuCl}_2 + \text{H}_2\text{SO}_4 \\ \text{CuCl}_2 + \text{Cu} &\longrightarrow \text{Cu}_2\text{Cl}_2 \end{aligned}$$

(iii) by heating cupric chloride with zinc or sulphur dioxide.

$$2CuCl_2 + Zn \longrightarrow Cu_2Cl_2 + ZnCl_2$$
 
$$2CuCl_2 + 2H_2O + SO_2 \longrightarrow Cu_2Cl_2 + 2HCl + H_2SO_4$$

(iv) by passing SO<sub>2</sub> through the solution containing copper sulphate and sodium chloride.

$$2CuSO4 + 2NaCl + 2H2O + SO2 \longrightarrow Cu2Cl2 + Na2SO4 + 2H2SO4$$

### Properties

(i) It is a white solid. It is insoluble in water but soluble in excess of hydrochloric acid.

$$Cu_2Cl_2 + 4HCl \longrightarrow 2H_2CuCl_3$$
 or 
$$Cu_2Cl_2 + 6HCl \longrightarrow 2H_3CuCl_4$$

The solution again gives a white precipitate on dilution.

(ii) It gradually turns green on exposure in air due to oxidation.

$$2Cu_2Cl_2 + 2H_2O + O_2 \longrightarrow 2[CuCl_2 \cdot Cu(OH)_2]$$
 Basic cupric chloride

(iii) The solution of cuprous chloride in HCl is oxidised by air or oxidising agents into cupric chloride.

$$Cu_2Cl_2 + 2HCl + \frac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O$$

(iv) The solution of cuprous chloride in HCl absorbs carbon monoxide and forms an addition compound.

$$Cu_2Cl_2 + 2CO \longrightarrow 2CuCl\cdot CO$$

The addition compound decomposes on heating evolving carbon monoxide. The reaction is utilised for the removal of carbon monoxide.

- (v) It dissolves in aqueous ammonia forming a colourless solution due to the formation of the complex Cu(NH<sub>3</sub>)<sub>2</sub>Cl.
- (vi) The ammonical cuprous chloride solution absorbs acetylene to form bright red precipitate of cuprous acetylide,  $Cu_2C_2$ .

$$2Cu(NH_3)_2Cl + C_2H_2 \longrightarrow Cu_2C_2 + 2NH_3 + 2NH_4Cl$$

Acetylene can be regenerated by treating the acetylide with strong HCl. The reaction is, therefore, used for the purification and separation of acetylene.

$$Cu_2C_2 + 2HCl \longrightarrow C_2H_2 + Cu_2Cl_2$$

(vii) Cuprous chloride with caustic alkalies gives a yellow precipitate of cuprous oxide which gradually changes to red.

$$\begin{array}{c} Cu_2Cl_2 + 2NaOH \longrightarrow & Cu_2O \\ & & Yellow \ changing \\ & to \ red \end{array} + 2NaCl + H_2O \\$$

(viii) With H<sub>2</sub>S, cuprous chloride forms a black precipitate of cuprous sulphide.

$$Cu_2Cl_2 + H_2S \longrightarrow Cu_2S + 2HCl$$

(ix) With sodium chloride or potassium chloride solution cuprous chloride forms a soluble complex.

$$Cu_2Cl_2 + 6NaCl \longrightarrow 2Na_3CuCl_4$$
  
 $Cu_2Cl_2 + 6KCl \longrightarrow 2K_3CuCl_4$ 

(x) Dry cuprous chloride forms addition compounds with ammonia gas of the formula CuCl·nNH $_3$  where  $n=1,\,1\frac{1}{2}$ , 3.

$$Cu_2Cl_2 + 2NH_3 \longrightarrow 2CuCl \cdot NH_3$$

#### Uses

- (i) Ammonical solution of cuprous chloride is used for absorbing acetylene.
- (ii) HCl solution of cuprous chloride is used for absorption of carbon monoxide.
  - (iii) It is also used for absorption of ammonia gas.
- (iv) It is used as a catalyst in **Deacon's** process for the manufacture of chlorine gas.
- **2. Cupric compounds:** In which copper is divalent, cupric compounds are more stable, more common and generally more stable. Most of the *anhydrous cupric compounds* are colourless while the hydrated compounds are generally blue due to the

formation of blue hydrated ion,  $[Cu(H_2O)_4]^{2+}$  or  $[Cu(H_2O)_6]^{2+}$ . Compounds of  $Cu^{2+}$  ions are paramagnetic due to presence of one unpaired electron in 3d energy shell, *i.e.*, configuration of  $Cu^{2+}$  is  $3d^9$ . Some important cupric compounds are described here.

## Cupric Oxide, CuO

It is called black oxide of copper and is found in nature as tenorite.

## Preparation

It is prepared—

(i) by heating Cu<sub>2</sub>O in air or by heating copper for a long time in air (the temperature should not exceed above 1100°C).

$$Cu_2O + \frac{1}{2}O_2 \longrightarrow 2CuO$$

$$2Cu + O_2 \longrightarrow 2CuO$$

(ii) by heating cupric hydroxide,

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$

(iii) by heating copper nitrate,

$$2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$$

(iv) on a commercial scale, it is obtained by heating malachite which is found in nature.

$$CuCO_3 \cdot Cu(OH)_2 \longrightarrow 2CuO + CO_2 + H_2O$$

## Properties

- (a) It is black powder and stable to moderate heating.
- (b) The oxide is insoluble in water but dissolves in acids forming corresponding salts.

$$\begin{array}{c} \text{CuO} + 2\text{HCl} \longrightarrow \text{CuCl}_2 + \text{H}_2\text{O} \\ \text{CuO} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O} \\ \text{CuO} + 2\text{HNO}_3 \longrightarrow \text{Cu(NO}_3)_2 + \text{H}_2\text{O} \end{array}$$

(c) When heated to 1100–1200°C, it is converted into cuprous oxide with evolution of oxygen.

$$4CuO \longrightarrow 2Cu_2O + O_2$$

(d) It is reduced to metallic copper by reducing agents like hydrogen, carbon and carbon monoxide.

$$\begin{array}{c} CuO + H_2 \longrightarrow Cu + H_2O \\ CuO + C \longrightarrow Cu + CO \\ CuO + CO \longrightarrow Cu + CO_2 \end{array}$$

#### **Uses**

It is used to impart green to blue colour to glazes and glass. It is used in organic analysis for the estimation and detection of carbon. It is also used in petroleum for the removal of sulphur.

## Cupric Chloride, CuCl<sub>2</sub>·2H<sub>2</sub>O

### Preparation

(i) The metal or cupric oxide or cupric hydroxide or copper carbonate is dissolved in conc. HCl. The resulting solution on crystallisation gives green crystals of hydrated cupric chloride.

$$2Cu + 4HCl + O_2 \longrightarrow 2CuCl_2 + 2H_2O$$

$$CuO + 2HCl \longrightarrow CuCl_2 + H_2O$$

$$Cu(OH)_2CuCO_3 + 4HCl \longrightarrow 2CuCl_2 + 3H_2O + CO_2$$

(ii) Anhydrous cupric chloride is obtained as a dark brown mass when copper metal is heated in excess of chlorine gas or by heating hydrated cupric chloride in HCl gas at 150°C.

$$Cu + Cl_2 \longrightarrow CuCl_2$$

$$CuCl_2 \cdot 2H_2O \xrightarrow{150^{\circ}C} CuCl_2 + 2H_2O$$

### Properties

- (i) It is a deliquescent compound and is readily soluble in water. The dilute solution is blue but concentrated solution is, however, green. It changes to yellow when conc. HCl is added. The blue colour is due to complex cation  $[Cu(H_2O)_4]^{2+}$  and yellow colour due to complex anion  $[CuCl_4]^{2-}$  and green when both are present.
  - (ii) The aqueous solution is acidic due to its hydrolysis.

$$CuCl_2 + 2H_2O \rightleftharpoons Cu(OH)_2 + 2HCl$$

(iii) The anhydrous salt on heating forms Cu<sub>2</sub>Cl<sub>2</sub> and Cl<sub>2</sub>.

$$2CuCl_2 \longrightarrow Cu_2Cl_2 + Cl_2$$

while the hydrated salt on strong heating gives CuO,  $Cu_2Cl_2$ , HCl and  $Cl_2$ .

$$3CuCl_2 \cdot 2H_2O \longrightarrow CuO + Cu_2Cl_2 + 2HCl + Cl_2 + 5H_2O$$

(iv) It is readily reduced to Cu<sub>2</sub>Cl<sub>2</sub> by copper turnings, or SO<sub>2</sub> gas, or hydrogen (Nascent-obtained by the action of HCl on Zn) or SnCl<sub>2</sub>.

$$\begin{aligned} & \text{CuCl}_2 + \text{Cu} \longrightarrow \text{Cu}_2\text{Cl}_2 \\ 2\text{CuCl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Cu}_2\text{Cl}_2 + 2\text{HCl} + \text{H}_2\text{SO}_4 \\ 2\text{CuCl}_2 + 2\text{H} \longrightarrow \text{Cu}_2\text{Cl}_2 + 2\text{HCl} \\ 2\text{CuCl}_2 + \text{SnCl}_2 \longrightarrow \text{Cu}_2\text{Cl}_2 + \text{SnCl}_4 \end{aligned}$$

(v) A pale blue precipitate of basic cupric chloride, CuCl<sub>2</sub>·3Cu(OH)<sub>2</sub> is obtained when NaOH is added.

$$CuCl_2 + 2NaOH \longrightarrow Cu(OH)_2 + 2NaCl$$
  
 $CuCl_2 + 3Cu(OH)_2 \longrightarrow CuCl_2 \cdot 3Cu(OH)_2$ 

It dissolves in ammonium hydroxide forming a deep blue solution. On evaporating of this solution deep blue crystals of tetrammine cupric chloride are obtained.

$$CuCl_2 + 4NH_4OH \longrightarrow Cu(NH_3)_4Cl_2\cdot H_2O + 3H_2O$$

#### Uses

It is used as a catalyst in Deacon's process. It is also used in medicines and as an oxygen carrier in the preparation of organic dyestuffs.

## Copper Sulphate (Blue Vitriol), CuSO<sub>4</sub>·5H<sub>2</sub>O

Copper sulphate is the most common compound of copper. It is called as *blue vitriol* or *nila thotha*.

### Preparation

(i) Copper sulphate is prepared in the laboratory by dissolving cupric oxide or hydroxide or carbonate in dilute sulphuric acid. The solution is evaporated and crystallised.

$$CuO + H2SO4 \longrightarrow CuSO4 + H2O$$

$$Cu(OH)2 + H2SO4 \longrightarrow CuSO4 + 2H2O$$

$$Cu(OH)2CuCO3 + 2H2SO4 \longrightarrow 2CuSO4 + 3H2O + CO2$$

(ii) On a commercial scale, it is prepared from scrap copper. The scrap copper is placed in a perforated lead bucket which is dipped into hot dilute sulphuric acid. Air is blown through the acid. Copper sulphate is crystallised from the solution.

$$Cu + H_2SO_4 + \frac{1}{2}O_2(air) \longrightarrow CuSO_4 + H_2O$$

## Properties

- (a) It is a blue crystalline compound and is fairly soluble in water.
- (b) Heating effect: CuSO<sub>4</sub>·5H<sub>2</sub>O crystals effloresce on exposure and converted into a pale blue powder, CuSO<sub>4</sub>·3H<sub>2</sub>O. When heated to 100°C, bluish white monohydrate CuSO<sub>4</sub>·H<sub>2</sub>O is formed. The monohydrate loses last molecule of water at 230°C giving the anhydrous salt, CuSO<sub>4</sub>, which is white.

Anhydrous copper sulphate (white) regains its blue colour when moistened with a drop of water (test of water).

If the anhydrous salt is heated at 720°C, it decomposes into cupric oxide and sulphur trioxide.

$$\begin{array}{c} \text{CuSO}_4 \xrightarrow{\phantom{-}720^{\circ}\text{C}} \text{CuO} + \text{SO}_3 \\ \downarrow \\ \text{SO}_2 + \frac{1}{2}\text{O}_2 \end{array}$$

(c) Action of NH<sub>4</sub>OH: With ammonia solution, it forms the soluble blue complex. First it forms a precipitate of Cu(OH)<sub>2</sub> which dissolves in excess of ammonia solution.

$$\begin{array}{c} CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2 + (NH_4)_2SO_4 \\ Cu(OH)_2 + 2NH_4OH + (NH_4)_2SO_4 \longrightarrow Cu(NH_3)_4SO_4 + 4H_2O \\ & \text{Tetrammine cupric} \\ & \text{sulphate} \end{array}$$

The complex is known as Schwitzer's reagent which is used for dissolving cellulose in the manufacture of artificial silk.

(d) Action of alkalies: Alkalies form a pale blue precipitate of copper hydroxide.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

(e) Action of potassium iodide: First cupric iodide is formed which decomposes to give white cuprous iodide and iodine.

$$[CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4] \times 2$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

(f) Action of potassium cyanide: First cupric cyanide is formed which decomposes to give cuprous cyanide and cyanogen gas. Cuprous cyanide dissolves in excess of potassium cyanide to form a complex, potassium cupro cyanide [K<sub>3</sub>Cu(CN)<sub>4</sub>].

$$[CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4] \times 2$$

$$2Cu(CN)_2 \longrightarrow Cu_2(CN)_2 + (CN)_2$$

$$Cu_2(CN)_2 + 6KCN \longrightarrow 2K_3Cu(CN)_4$$

$$2CuSO_4 + 10KCN \longrightarrow 2K_3Cu(CN)_4 + 2K_2SO_4 + (CN)_2$$

(g) Action of potassium ferrocyanide: Reddish brown precipitate of cupric ferrocyanide is formed. (test of Cu<sup>2+</sup> ion)

$$2\text{CuSO}_4 + \text{K}_4\text{Fe}(\text{CN})_6 \longrightarrow \text{Cu}_2\text{Fe}(\text{CN})_6 + 2\text{K}_2\text{SO}_4$$

(h) Addition of electropositive metals: Electropositive elements like zinc and iron precipitate copper from a solution of copper sulphate.

$$CuSO_4 + Fe \longrightarrow Cu + FeSO_4$$
  
 $CuSO_4 + Zn \longrightarrow Cu + ZnSO_4$ 

(i) Action of  $H_2S$ : When  $H_2S$  is passed through copper sulphate solution, a black precipitate of copper sulphide is formed.

$$CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4$$

The black precipitate dissolves in conc. HNO<sub>3</sub>.

$$3\text{CuS} + 8\text{HNO}_3 \longrightarrow 3\text{Cu(NO}_3)_2 + 2\text{NO} + 3\text{S} + 4\text{H}_2\text{O}$$

(j) Action of potassium sulphocyanide: Cupric sulphocyanide is formed.

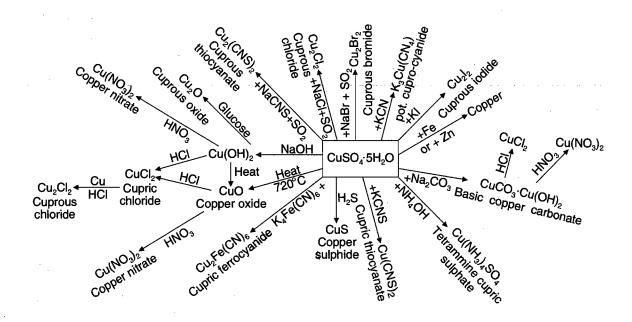
$$CuSO_4 + 2KCNS \longrightarrow Cu(CNS)_2 + K_2SO_4$$

If SO<sub>2</sub> is passed through the solution, a white precipitate of cuprous sulphocyanide is formed.

$$2\text{CuSO}_4 + 2\text{KCNS} + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Cu}_2(\text{CNS})_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$$

[This is the general method for obtaining cuprous compounds.]

(k) **Double sulphates:** Copper sulphate forms double salts with alkali sulphate  $K_2SO_4$ ·Cu $SO_4$ ·6H $_2O$  and with ammonium sulphate as  $(NH_4)_2SO_4$ ·Cu $SO_4$ ·6H $_2O$ .



PROPERTIES OF COPPER SULPHATE AND PREPARATION OF VARIOUS COPPER COMPOUNDS

(1) Action of sodium thiosulphate: Sodium thiosulphate reacts with copper sulphate to form cupric thiosulphate which is reduced by sodium thiosulphate. The cuprous compound thus formed dissolves in excess of sodium thiosulphate to form a complex.

#### **■** Uses

- (i) Copper sulphate is used for the preparation of other copper compounds.
- (ii) It finds use in electroplating, electrotyping, calicoprinting and dyeing.
- (iii) It is used in agriculture as a fungicide and germicide.

  Bordeaux mixture consisting copper sulphate and lime is used to kill moulds and fungi on vines, trees, potatoes, etc.
- (iv) It is used as a laboratory reagent especially in the preparation of Fehling's solution.
  - (v) It finds use as an antiseptic in medicine.
  - (vi) It is extensively used in electric batteries.

# 14.17 SILVER

**Occurrence:** Silver is a rare element as it forms only  $10^{-8}$  per cent of the earth's crust. However, it was known in prehistoric times and used for its colour and beauty as a precious metal. Silver is found in nature in two forms.

#### 1. Native State

It occurs in the metallic condition usually associated with copper, gold and platinum metals. Native silver has been reported in a few places in Canada, United States of America, Mexico and Peru.

#### 2. Combined State

The important ores of silver are:

- (a) In the form of sulphide:
- (i) Argentite or silver glance, Ag<sub>2</sub>S
- (ii) Pyrargyrite or Ruby silver, 3Ag<sub>2</sub>S·Sb<sub>2</sub>S<sub>3</sub>
- (iii) Stromeyerite or silver copper glance, (Cu, Ag)<sub>2</sub>S
- (iv) Silver is also associated in the form of Ag<sub>2</sub>S in the lead ore, galena (PbS). The lead extracted usually contains silver and called argentiferous lead. Silver is recovered before lead is put into use.

#### (b) In the form of halide:

Chlorargyrite or Horn silver, AgCl.

In India, it occurs mainly as Ag<sub>2</sub>S associated with lead and zinc ores at Bawdivin and also associated with gold, in the native gold ores of Kolar. From these, silver is obtained as a

by-product but no workable deposits of silver are found in India

The ores of silver are usually associated with large amounts of rock, silica and clay. The silver content hardly exceeds 1.0 per cent. Most of the silver (nearly four-fifth of the total production) is obtained from argentiferous lead and from the anodic mud formed during electrolytic refining of copper. Thus, silver is obtained from the following sources.

- (i) From the ores of silver
- (ii) From native silver
- (iii) From argentiferous lead
- (iv) From the anodic mud in copper refining.

# 2 1. Extraction of silver from argentite ore (Cyanide process)

Cyanide process is the modern process for the extraction of silver. The process is also called as Mac-Arthur and Forest process. It is based on two points.

- (i) Silver compounds (or even free silver) dissolve in sodium cyanide solution forming a complex salt, NaAg(CN)<sub>2</sub>, in presence of air.
- (ii) Silver is precipitated from this complex salt by the addition of zinc.

The process involves the following steps:

- (i) Concentration of the ore: Concentration of the ore is done by froth floatation process. The ore is crushed and taken in a tank filled with water to which pine oil and potassium xanthate have been added. The whole mixture is agitated by passing a strong stream of air. The ore particles come to the surface alongwith froth while silicious impurities settle to the bottom.
- (ii) Cyanidation: The concentrated ore is ground to a very fine powder in ball mill. The finely powdered ore is treated with dilute solution (0.4 to 0.6%) of sodium cyanide and a current of air is blown through the whole mass. The silver present in the ore dissolves in the solution slowly to form sodium argentocyanide.

$$Ag_2S + 4NaCN \rightleftharpoons 2NaAg(CN)_2 + Na_2S$$

The above reaction is reversible. The air which is blown in serves an important function in removing sodium sulphide from the equilibrium mixture and causing the reaction to proceed in the desired direction.

$$4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$$

The soluble sodium argentocyanide is removed by filtration. [Metallic silver and silver chloride (Horn silver) also dissolve in sodium cyanide solution.

$$4Ag + 8NaCN + 2H_2O + O_2 (air) \longrightarrow 4NaAg(CN)_2 + 4NaOH$$

$$AgCl + 2NaCN \longrightarrow NaAg(CN)_2 + NaCl]$$

(iii) **Recovery of silver:** Silver is precipitated from the solution by addition of zinc powder in a finely divided condition.

Silver is precipitated as a dark amorphous mass while zinc goes into the complex.

2NaAg(CN)<sub>2</sub> + Zn 
$$\longrightarrow$$
 Na<sub>2</sub>Zn(CN)<sub>4</sub> + 2Ag
Sodium zinco-
cvanide

[Zinc is more electropositive than silver.]

The precipitated silver is removed by filtration, dried and fused with potassium nitrate in a crucible in furnace. The impurities are oxidised and rise as a scum on the surface. Liquid silver on cooling appears as compact mass.

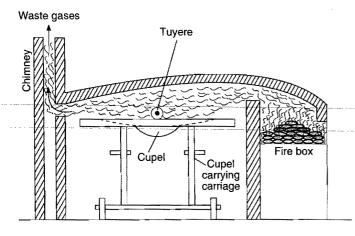


Fig. 14.13

- (iv) **Refining:** The main impurities are of lead, copper and gold. These are removed by following methods.
- (a) Cupellation process: Cupel is a big oval dish with a shallow hearth and is made of bone-ash or porous cement. The impure silver is fused on the hearth of the cupellation furnace and a strong current of air is blown over it.

Lead is oxidised to lead oxide (Litharge: PbO) which is blown away by air. Other impurities are also oxidised and rise to the surface and removed as scum. The oxides may also be absorbed by the lining of the cupel. The completion of the process is indicated by the appearance of bright shining surface of the molten silver.

(b) Electrolytic process: The impure silver is made as anode and pure silver plate as cathode. The electrolytic solution is of silver nitrate containing 10% nitric acid. On passing electric current silver ions start depositing on cathode and equivalent amount from anode comes into solution. In this way silver is transferred from anode to cathode. Copper goes into solution as copper nitrate while gold collects below the anode as anodic mud.

## 2. Amalgamation process

This is the old method of extraction. It is still in use in some countries. The sulphide ore is crushed and converted into a slime with a solution of cupric chloride.

$$Ag_2S + CuCl_2 \longrightarrow 2AgCl + CuS$$

Some mercury is then added to the product. Silver chloride reacts with mercury liberating silver.

$$2AgCl + 2Hg \longrightarrow 2Ag + Hg_2Cl_2$$

#### FLOW SHEET FOR THE EXTRACTION OF SILVER

Silver ore (Argentite)

**CYANIDATION** 

Concentrated ore + NaCN solution (0.4-0.6%) + Air  $Ag_2S + 4NaCN \implies 2NaAg(CN)_2 + Na_2S$  $4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$ 

↓ Filtrate

PRECIPITATION OF SILVER WITH ZINC  $2NaAg(CN)_2 + Zn \longrightarrow 2Ag + Na_2Zn(CN)_4$  Black ppt.

Black ppt. of Ag + KNO<sub>3</sub>  $\xrightarrow{\text{Fuse}}$  Compact mass (Silver metal)

#### **ELECTROLYTIC REFINING**

Anode: Impure silver
Cathode: Pure silver plate

Electrolyte: AgNO<sub>3</sub> solution + HNO<sub>3</sub> Pure silver deposited on the cathode

The silver dissolves in excess of mercury to form an amalgam. It is washed and then distilled when silver is left behind in the retorts.

# 3. Extraction of silver from argentiferous lead (Desilverisation of lead)

Lead ores, especially galena, contain a very small percentage of silver sulphide. During the extraction of lead, silver remains in the metal. On account of its high value, silver is removed from the lead before it is used for any purpose. The crude lead contains upto 2% of silver. This poor amount of silver requires to be concentrated before desilverisation. The recovery of silver from crude lead (argentiferous lead), thus involves two steps:

- (i) Partial separation of lead (a) by Pattinson's process or(b) by Parkes process.
- (ii) Removal of lead as lead oxide by cupellation process.
- (a) Pattinson's process: This process is based on the fact that silver-lead system has an eutectic mixture with 2.6% silver melting at 303°C whereas pure lead melts at 327°C.

When the molten argentiferous lead is allowed to cool slowly, crystals of pure lead are deposited until the silver content of the mixture has risen to 2.6%. The crystals of pure lead are removed with the help of perforated ladles. The alloy rich in silver content is then subjected to cupellation to remove the remaining lead.

- **(b) Parkes process:** This is at present the most commonly used method. It depends on the following points:
  - (i) Zinc and lead are not miscible.
  - (ii) Silver is more miscible with zinc than lead.
- (iii) Zinc-silver alloy is lighter than molten lead and have a higher melting point.

Lead containing silver is melted in large pots. Zinc dust to the extent of only 1% is added and thoroughly stirred. The temperature is raised above the melting point of zinc. Zinc dissolves silver and comes up on the surface where zinc-silver alloy forms a crust. This is skimmed off by perforated ladles. More zinc is added and the operation is repeated for several times till lead shows almost no trace of dissolved silver. It is possible to reduce the silver content to 0.0005%.

The zinc-silver alloy containing some lead is now distilled with a little charcoal when zinc distills over. The recovered zinc is used again. The lead silver alloy left behind is now put to cupellation as to remove lead. The pure silver is, thus, obtained.

# 4. Recovery of silver from anodic mud of copper refining

The mud is treated with nitric acid and the solution is filtered. The filtrate contains nitrates of silver and lead. To the filtrate HCl is then added when silver and lead settle down as chlorides in the form of white precipitate. The chlorides are separated, dried and fused with sodium carbonate in a crucible when an alloy of Ag and Pb is obtained. To remove lead, the alloy is put to cupellation.

Anodic mud + HNO<sub>3</sub> 
$$\longrightarrow$$
 Nitrates of Ag and Pb (Filtrate)
$$\downarrow + \text{HCl}$$

$$Ag \xrightarrow{\text{Cupellation}} Ag \xrightarrow{\text{Pb}} \text{Pb} \xleftarrow{\text{Fused}} Ag\text{Cl} \cdot \text{PbCl}_2$$

$$Pb(NO_3)_2 + 2\text{HCl} \longrightarrow Pb\text{Cl}_2 + 2\text{HNO}_3$$

$$AgNO_3 + \text{HCl} \longrightarrow Ag\text{Cl} + \text{HNO}_3$$

$$Pb\text{Cl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow Pb + 2\text{NaCl} + \text{CO}_2 + \frac{1}{2}\text{O}_2$$

$$2\text{AgCl} + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{Ag} + 2\text{NaCl} + \text{CO}_2 + \frac{1}{2}\text{O}_2$$

#### 5. Silver from coins or ornaments

Coins and ornaments are alloys of silver and copper. The alloy is treated with nitric acid. Both copper and silver go into

the solution in the form of nitrates. The excess of nitric acid is boiled and the solution is treated with dil. HCl when a white precipitate of silver chloride is obtained. This is separated and converted into silver by any of the following methods.

(a) Silver chloride is fused with sodium carbonate in a crucible.

$$2AgCl + Na_2CO_3 \xrightarrow{Fuse} 2Ag + 2NaCl + CO_2 + \frac{1}{2}O_2$$

(b) The precipitate of AgCl is reduced with nascent hydrogen produced by the action of zinc and dilute H<sub>2</sub>SO<sub>4</sub>.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$
  
 $AgCl + H \longrightarrow Ag + HCl$ 

(c) AgCl is dissolved in potassium cyanide solution when a complex salt, potassium argento-cyanide is formed.

$$AgCl + 2KCN \longrightarrow KAg (CN)_2 + KCl$$

Ag is obtained from the solution by addition of zinc.

$$2KAg(CN)_2 + Zn \longrightarrow K_2Zn(CN)_4 + 2Ag$$
 Soluble

(d) By boiling silver chloride with caustic soda and glucose.

$$\begin{array}{c} 2AgCl + 2NaOH \longrightarrow Ag_2O + 2NaCl + H_2O \\ \\ Ag_2O + C_6H_{12}O_6 \longrightarrow 2Ag + C_6H_{12}O_7 \\ \\ \\ Glucose \\ \end{array}$$

The silver thus obtained, is purified by fusion with borax and nitre followed by electrolytic purification.

**Separation of silver from gold:** The separation of silver and gold is technically known as parting. This is done by following methods:

(a) Parting with sulphuric acid: The alloy having gold, less than 20%, is treated with boiling concentrated sulphuric acid. Silver dissolves as silver sulphate and gold remains as spongy mass. The solution is diluted with water and the solution is filtered. The filtrate is then treated with scrap iron or copper or zinc to separate silver.

$$Ag_2SO_4 + Zn \longrightarrow 2Ag + ZnSO_4$$

If the percentage of gold in the alloy is more than 20%, some silver is added to alloy as to reduce the percentage of gold less than 20% and then the process of parting is applied.

(b) Parting with 'Moebius' electrolytic process: The alloy of silver and gold is made the anode while pure silver plate as cathode. The electrolytic solution consists of a dilute solution of silver nitrate acidified with nitric acid. On passing electric current silver dissolves from the anode and deposits on the cathode. Gold remains undissolved and deposits as a slime in canvas bags surrounding the anode.

$$AgNO_{3}$$

$$\downarrow \downarrow$$

$$Ag^{+} + e \longrightarrow Ag \text{ cathode} \longleftarrow Ag^{+} + NO_{3}^{-} \longrightarrow Ag \text{ anode}$$

$$NO_{3}^{-} + Ag \longrightarrow AgNO_{3} + e$$

#### Properties

**Physical:** (a) It is a lustrous white metal. It melts at 961°C and boils at 2180°C. Its specific gravity is 10.5. (b) It is very good conductor of heat and electricity (better than even copper). (c) On heating, the molten mass absorbs oxygen which is again released on cooling. This property is called **spitting of silver.** (d) It is hard, malleable and ductile.

Chemical: (a) Action of atmosphere: Silver remains untarnished in air free from hydrogen sulphide. Air contaminated with hydrogen sulphide covers it with an adherent film of black silver sulphide.

$$2Ag + H_2S \longrightarrow Ag_2S + H_2$$

- **(b) Action of oxygen and water:** Silver is not affected by oxygen and water.
- (c) Action of halogens: Silver combines slowly with free halogens even at room temperature. The reaction is rapid at red heat.

$$2Ag + X_2 \longrightarrow 2AgX \quad (X_2 = Cl_2, Br_2 \text{ or } I_2)$$

(d) Action of acids: Silver is not affected by dilute and concentrated hydrochloric acid. It is also not acted upon by dilute sulphuric acid.

In concentrated sulphuric acid, silver dissolves on heating with evolution of sulphur dioxide.

$$\frac{\text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{O} + \text{SO}_2 + \text{O}}{2\text{Ag} + \text{H}_2\text{SO}_4 + \text{O} \longrightarrow \text{Ag}_2\text{SO}_4 + \text{H}_2\text{O}}$$

$$\frac{2\text{Ag} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Ag}_2\text{SO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}}{2\text{Ag} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Ag}_2\text{SO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}}$$

Silver dissolves in both dilute and concentrated nitric acids.

Dilute HNO<sub>3</sub>: 
$$2HNO_3 \longrightarrow H_2O + 2NO + 3[O]$$

$$[2Ag + 2HNO_3 + O \longrightarrow 2AgNO_3 + H_2O] \times 3$$

$$6Ag + 8HNO_3 \longrightarrow 6AgNO_3 + 2NO + 4H_2O$$
or  $3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO + 2H_2O$ 
Conc. HNO<sub>3</sub>:  $2HNO_3 \longrightarrow H_2O + 2NO_2 + O$ 

$$2Ag + 2HNO_3 + O \longrightarrow 2AgNO_3 + H_2O$$
or  $Ag + 2HNO_3 \longrightarrow AgNO_3 + NO_2 + 2H_2O$ 

- (e) Action of alkalies: Alkalies have no action on silver even when fused.
- (f) Action of alkali cyanides: Silver dissolves in the solution of alkali cyanides in the presence of oxygen forming the complex argentocyanide.

$$4Ag + 8KCN + 2H2O + O2 \longrightarrow 4K[Ag(CN)2] + 4KOH$$

$$4Ag + 8NaCN + 2H2O + O2 \longrightarrow 4Na[Ag(CN)2] + 4NaOH$$

#### **■** Uses

(i) Silver is used in making coins, ornaments, silver-ware, decoration pieces, etc. Pure silver is too soft to be used for these purposes and is, therefore, alloyed generally with copper.

Silver ornaments and utensils usually contain 80% silver and 20% copper. A silver coin has generally the composition Ag 50%, Cu 40%, Zn 5% and Ni 5%.

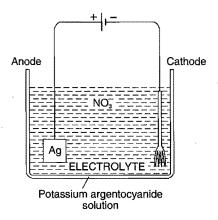


Fig. 14.14

(ii) Silver is used for plating articles of base-metals. The article to be plated is made the cathode while the anode consists of pure silver. The electrolyte is the solution of potassium argentocyanide. As the complex ion is very stable, the concentration of silver ion in solution is very small at any time.

$$[Ag(CN)_2]^- \iff Ag^+ + 2CN^-$$

Silver is deposited slowly and uniformly when electricity is passed through the solution.

- (iii) Silver amalgam is used in filling teeth and in silvering mirrors.
- (iv) Silver leaves are used in Ayurvedic and Yunani medicines.
- (v) It is used for making silver salts used in silvering of mirrors, photography and medicine.

# 14.18 COMPOUNDS OF SILVER

# Silver nitrate (Lunar caustic), AgNO<sub>3</sub>

Silver nitrate is the most common and important salt of silver.

#### Preparation

It is prepared by heating silver with dilute nitric acid. The solution is concentrated and cooled when the crystals of silver nitrate separate out.

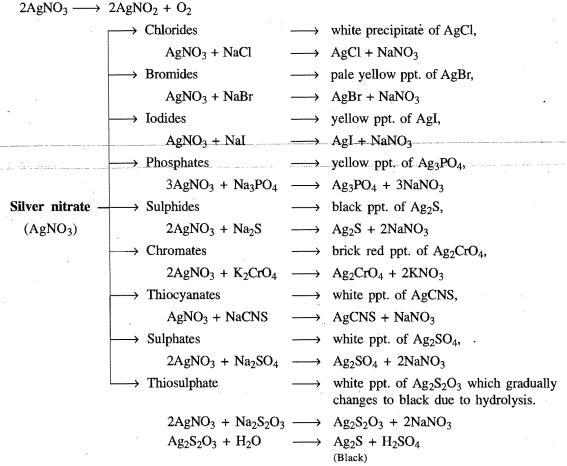
$$3Ag + 4HNO_3 \xrightarrow{Heat} 3AgNO_3 + NO + 2H_2O$$

#### Properties

- (a) It is a colourless crystalline compound, soluble in water and alcohol. It melts at 212°C.
- (b) In contact with organic substances it blackens due to decomposition into metallic silver. Thus, it leaves black stains

when comes in contact with skin and clothes. It produces burning sensation like caustic and leaves a white stain (usually a black stain) like the moon luna on skin and thus, called Lunar caustic. It is decomposed by light also and therefore stored in coloured bottles.

(c) On heating above its melting point, it decomposes to silver nitrite and oxygen.



On account of these reactions, silver nitrate is an excellent laboratory reagent for the identification of various acidic radicals.

- (e) Solid AgNO<sub>3</sub> absorbs ammonia gas with the formation of an addition compound, AgNO<sub>3</sub>·2NH<sub>3</sub>.
- (f) When treated with a solution of NaOH, it forms precipitate of silver oxide. Originally, it has brown colour but turns black when dried.

$$2AgNO_3 + 2NaOH \longrightarrow Ag_2O + 2NaNO_3 + H_2O$$

(g) When KCN is added to silver nitrate, a white precipitate of silver evanide appears which dissolves in excess of KCN forming a complex salt, potassium argento cyanide.

$$\begin{array}{ccc} \text{AgNO}_3 + \text{KCN} & \longrightarrow & \text{AgCN} + \text{KNO}_3 \\ \text{AgCN} + \text{KCN} & \longrightarrow & \text{KAg(CN)}_2 \\ & & \text{Potassium argentocyanide} \end{array}$$

(h) When sodium thiosulphate is added to silver nitrate, a white precipitate of silver thiosulphate appears. This precipitate, however, dissolves in excess of sodium thiosulphate forming a complex salt.

When heated at red heat, it further decomposes to metallic silver.

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

(d) Solutions of halides, phosphates, sulphides, chromates, thiocyanates, sulphates and thiosulphates, all give a precipitate of the corresponding silver salt with silver nitrate solution.

 $AgNO_3 + NaI \longrightarrow AgI + NaNO_3$  $\rightarrow$  yellow ppt. of Ag<sub>3</sub>PO<sub>4</sub>,

- (i) AgNO<sub>3</sub> reacts with iodine in two ways:
- (a)  $6AgNO_3$  (excess) +  $3I_2$  +  $3H_2O \longrightarrow$  $AgIO_3 + 5AgI + 6HNO_3$

(b) 
$$5AgNO_3 + 3I_2$$
 (excess)  $+ 3H_2O \longrightarrow HIO_3 + 5AgI + 5HNO_3$ 

(j) Silver is readily displaced from an aqueous silver nitrate solution by the base metals, particularly, if the solution is somewhat acidic,

$$2AgNO_3 + Cu \longrightarrow 2Ag + Cu(NO_3)_2$$
  
 $2AgNO_3 + Zn \longrightarrow 2Ag + Zn(NO_3)_2$ 

(k) Phosphine, arsine and stibine all precipitate silver from silver nitrate solution.

$$PH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3PO_3$$

$$AsH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3AsO_3$$

(l) All halogen acids, except HF, precipitate silver halides from aqueous solution of AgNO<sub>3</sub>.

$$AgNO_3 + HX \longrightarrow AgX + HNO_3$$

(m) When NH<sub>4</sub>OH is added to silver nitrate solution, a brown precipitate of silver oxide appears which dissolves in excess of ammonia forming a complex salt.

$$2 AgNO_3 + 2NH_4OH \longrightarrow Ag_2O + 2NH_4NO_3 + H_2O$$
 
$$Ag_2O + 2NH_4NO_3 + 2NH_4OH \longrightarrow 2[Ag(NH_3)_2]NO_3 + 3H_2O$$

The ammonical solution of AgNO<sub>3</sub> gives the following reactions:

(a) It reacts with acetylene to form white compound, silver acetylide.

$$2AgNO_3 + 2NH_4OH + C_2H_2 \longrightarrow Ag_2C_2 + 2NH_4NO_3 + 2H_2O$$
  
Silver acetylide

(b) It converts glucose to gluconic acid.

$$Ag_2O + C_6H_{12}O_6 \longrightarrow 2Ag + C_6H_{12}O_7$$

(c) It oxidises formaldehyde to formic acid.

$$Ag_2O + HCHO \longrightarrow 2Ag + HCOOH$$

## Uses

- (i) It is used as a laboratory reagent for the identification of various acidic radicals especially for chloride, bromide and iodide. The ammonical silver nitrate solution, *i.e.*, Tollen's reagent is used in organic chemistry for testing aldehydes, reducing sugars, etc.
- (ii) Silver nitrate used for making silver halides which are used in photography.
- (iii) It is used in the preparation of making inks and hair dyes.
- (iv) A very dilute solution is used in causterisation of eyes. The salt is sometimes used as a dental antiseptic.
- (v) It is used extensively for the preparation of silver mirrors. The process of depositing a thin and uniform layer of silver on a clean glass surface is known as **silvering of mirrors**. It is employed for making looking glasses, concave mirrors and reflecting surfaces. The process is based on the reduction of ammonical silver nitrate solution by some reducing agent like formaldehyde, glucose, etc. The silver film deposited on the glass is first coated with a varnish and finally painted with red lead to prevent its being scraped off.

## Silver bromide, AgBr

## Preparation

It is prepared by the reaction of silver nitrate with a soluble bromide.

$$AgNO_3 + NaBr \longrightarrow AgBr + NaNO_3$$

### Properties

(a) It is a pale yellow solid. It is insoluble in water and concentrated acids. It is partially soluble in strong solution of ammonium hydroxide due to complex formation.

$$AgBr + 2NH_4OH \longrightarrow Ag(NH_3)_2Br + 2H_2O$$

- (b) On heating, it melts to a red liquid.
- (c) It is most sensitive to light. It undergoes photoreduction.

$$2AgBr \xrightarrow{Light} 2Ag + Br_2$$

(d) It dissolves in potassium cyanide.

AgBr + 2KCN 
$$\longrightarrow$$
 KAg(CN)<sub>2</sub> + KBr

Potassium argento-
cyanide (Soluble)

(e) It dissolves in sodium thiosulphate.

$$\begin{array}{c} AgBr + 2Na_2S_2O_3 \longrightarrow & Na_3[Ag(S_2O_3)_2] + NaBr \\ & Sodium \ argento- \\ & thiosulphate \ (Soluble) \end{array}$$

(f) AgBr is reduced to silver, when treated with zinc and dilute H<sub>2</sub>SO<sub>4</sub>.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$
  
 $2AgBr + 2H \longrightarrow 2Ag + 2HBr$ 

[Note: All above reactions are also observed in the case of AgCl. However, it is white and fairly soluble in ammonium hydroxide. It is sensitive to light.]

#### Uses

It is used for making photographic films and plates because it is sensitive to light.

## 14.19 GOLD

Occurrence: Gold is mainly found in native state either mixed with quartz in ancient rocks (vein gold) or scattered in sand and gravel (placer gold) or in the alluvial sand (alluvial gold) of certain rivers which pass over auriferous rocks. It is also found to a small extent in combined state as sulphide, telluride or arsenosulphide. The important sources of gold are:

- (i) Alluvial sand or gravel
- (ii) Calaverite AuTe<sub>2</sub>
- (iii) Sylvanite AuAgTe<sub>2</sub>

Mainly gold comes from the mines of South Africa. India produces about 2% of the total world production. **Kolar Mines** in Karnataka produce about 99% of our gold output.

**Extraction:** (i) From alluvial sa From alluvial sands, gold is recovered by making use of its high specific gravity (19.3). The oldest method is **pan washing.** In big pans made of iron or zinc, the gold bearing sand is agitated by giving a rotatory motion to the pan when the heavier gold particles settle down whereas the sand is washed away. This has now been replaced by placer mining.

Gold bearing sand is introduced in a sluice way system and powerful streams of water are passed over it. A **sluice way system** is an inclined channel made up of wood having a series of sluices, *i.e.*, troughs and cross wire strips known as riffles. The gold particles are retained in the sluice whereas sand particles are taken away by the water.

(ii) From auriferous quartz: The bigger pieces of auriferous quartz are crushed and broken into small pieces by rock crushers and then powdered by a battery of stamp mills working in series. The powdered ore is washed out of stamp mill by a current of water, when only fine particles can pass through the screen.

## Amalgamation process

The slurry from the stamp mill is passed over amalgamated copper plates placed just infront of stamp mills. The gold combines with mercury to form amalgam which is removed from the plates.

The amalgam is then distilled when the mercury passes over leaving behind gold. This process can remove 70-80% of the gold. The residual part is known as **tailings**.

The tailings or the concentrated ore of gold is put in large vats made of wood or cement having perforated false bottoms covered with coconut mattings. This is treated with 0.1% solution of NaCN in the presence of excess of air. The gold dissolves according to the following reaction.

$$4Au + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Au(CN)_2] + 4NaOH$$

The gold solution obtained is treated with zinc dust when gold being less electropositive gets precipitated.

$$2Na[Au(CN)_2]+Zn \longrightarrow Na_2Zn(CN)_4 + 2Au$$

The precipitated gold is recovered by filtration.

The crude gold contains silver, copper, zinc, lead, etc., as impurities. These impurities are removed by cupellation and parting process. Gold can be refined by electrolytic process also.

#### Fineness of Gold

Gold is a precious and noble metal. It is very stable towards common reagents and resists the action of the atmosphere. It is not attacked by air or oxygen or water at any temperature. Since it retains its bright surface untarnished, it is used for making ornaments, jewellery and watches. Generally, small quantities of other metals, especially copper, are added to the gold to make it harder. The purity or fineness of gold is generally expressed in **carats**, pure gold being known as 24 carats. Ornaments available these days are made of 18 carats. This is an alloy of gold containing 18 parts gold and 6 parts other metals.

Thus, percentage of gold in 18 carats is  $\frac{100}{24} \times 18$ , *i.e.*, 75 and the percentage of other metals is 25.

# 14.20 POSITION OF ZINC FAMILY IN PERIODIC TABLE

Group 12 (IIB) of the long form of periodic table consists of four elements namely zinc (Zn), cadmium (Cd), mercury (Hg), and ununbium(Uub)\*. These are collectively called as zinc metals as zinc is the predominant member. These elements are the end members of the four series of d-block elements as the last differentiating electron is accommodated on (n-1)d energy shell. Zinc is the last member of 3d series, cadmium is the last member of 4d series, mercury is the last member of 5d-series and ununbium is the last member of 6d series.

Group	IB (11)	11B	111A
Period		(12)	(13)
4	Cu	Zn	Ga
	(29)	(30)	(31)
5	Ag	Cd	In
	(47)	(48)	(49)
6	Au	Hg	Tl
	(79)	(80)	(81)
7	Uuu	Uub	Uut
	(111)	(112)	(113)

3d series Sc (Ist member,  $3d^1$ ) . . .Zn (last member,  $3d^{10}$ ) 4d series Y (Ist member,  $4d^1$ ) . . .Cd (last member,  $4d^{10}$ ) 5d series La (Ist member,  $5d^1$ ) . . .Hg (last member,  $5d^{10}$ ) 6d series Ac (Ist member,  $6d^1$ ) . . .Uub (last member,  $6d^{10}$ )

IIB group is present between IB (Transition elements) and IIIA (Normal elements). Thus, the elements of IIB show mixed properties of transition elements and normal elements. The inclusion of Zn, Cd, Hg and Uub in the same sub-group of the periodic table is justified by the similarities and gradation in their properties as the atomic number increases from Zn to Uub.

# 1. Electronic configuration

They have similar electronic configuration. The distribution of the electrons in various energy shells of these atoms is shown below:

Zn	30	2, 8, 18, 2	$3d^{10}$ , $4s^2$
Cd	48	2, 8, 18, 18, 2	4 $d^{10}$ , $5s^2$
Hg	80	2, 8, 18, 32, 18, 2	5 $d^{10}$ , $6s^2$
Uub	112	2, 8, 18, 32, 32, 18, 2	6 $d^{10}$ , $7s^2$

<sup>\*</sup>Ununbium is recently discovered synthetic radioactive element. Not much is known about its properties.

These configurations show that outermost shell has two electrons while the penultimate shell contains 18 electrons, *i.e.*, they have general configuration  $(n-1)d^{10}ns^2$ . Thus, these are d-block elements but do not show many properties which are shown by d-block elements. For example, (i) They do not show variable valency. (ii) Most of their compounds are colourless. (iii) Their melting and boiling points are very low. (iv) These are diamagnetic. (v) These are more electropositive as the oxidation potentials for zinc and cadmium being positive. This is due to the completion of (n-1)d energy shell which has 10 electrons (the maximum capacity of d-subshell).

### 2. Valency

All the elements show divalency as only  $ns^2$  electrons are lost by these elements.  $M^{2+}$  ions produced, possess  $(n-1)d^{10}$  configuration. This configuration is stable and hence cannot lose any more electrons. However, mercury forms two series of salts, viz., mercurous salts containing  $Hg_2^{2+}$  ion and mercuric salts containing  $Hg_2^{2+}$  ion. Both these ions show divalency of mercury. Mercurous ion does not exist as  $Hg^+$  but as  $Hg_2^{2+}$ . Thus, mercurous chloride exists as Cl-Hg-Hg-Cl and not as Hg-Cl.

#### 3. Occurrence

They do not occur in free state. All these metals occur as sulphides which constitute their important ores. Cadmium is usually found in the ores of zinc. However, mercury occurs in small quantities in the native state.

## 4. Physical characteristics

- (a) **Physical state:** Zinc and cadmium are solids while mercury is a liquid at ordinary temperature. The interatomic forces of attraction are considerably weak. These are so small in mercury that it exists in liquid state.
- (b) Melting and boiling points: The melting and boiling points are low as electrons from (n-1)d-shell are not available for bonding.

Element	Zn	Cd	Hg
M. pt. (°C)	419.5	320.9	-38.4
B. pt. (°C)	907	765	357

These metals are volatile in nature and easily come into vapour state.

atomic radii are fairly large, *i.e.*, more than coinage metals but less than alkaline earth metals. Atomic radii, atomic volume and density gradually increases from Zn to Hg.

Element	Zn	Cd	Hg
Atomic radii	1.25	1.41	1.44
Atomic volume	9.20	13.10	14.80
Density	7.10	8.60	13.60

(d) Ionisation energy and oxidation potential: These metals have fairly high values of ionisation energies. The values indicate that these metals should be less reactive. In fact, they are even more reactive than the coinage metals. This is due to their high values of oxidation potentials which are positive for Zn and Cd. The ionisation potential does not follow the regular trend. The electropositive nature and the chemical activity decreases from Zn to Hg. Hg is somewhat noble in nature.

Element	Zn	Cd	Hg
First ionisation potential (eV)	9.40	9.00	10.40
Oxidation potential (volt)	0.76	0.40	-0.85

(e) Other physical properties: All the three metals are good conductors of electricity. These are greyish white lustrous metals. These are malleable and ductile. The malleability and ductility decreases from Zn to Cd. Except Hg, other two metals are moderately hard.

# 5. Chemical nature of the metals and their compounds

(a) Action of air and water: The effect of atmosphere decreases from Zn to Hg. Zinc is slowly coated with a bluish white protective film of oxide in moist air, cadmium is much less affected while mercury is not affected at all.

Zinc decomposes boiling water slightly but at red heat, zinc decomposes steam easily. Cadmium resembles zinc but is much less reactive. Mercury is not affected under any conditions.

$$Zn + H_2O \longrightarrow ZnO + H_2$$

**(b) Action of oxygen:** All form oxides of the type *MO* when heated in air or oxygen. Basic properties increases. ZnO is amphoteric while CdO and HgO are basic in character. These are insoluble in water.

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$
 $ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$ 
Sodium zincate
 $HgO + H_2SO_4 \longrightarrow HgSO_4 + H_2O$ 

The stability of the oxides towards the action of heat decreases in the order of Zn, Cd, Hg. Zinc oxide and cadmium oxide sublime.HgO does not sublime because it decomposes on heating.

$$2HgO \longrightarrow 2Hg + O_2$$

The colours of these oxides are interesting. Zinc oxide is white at room temperature but turns yellow on heating. At high temperature metal excess non-stoichiometry is shown by ZnO. Cadmium oxide has chocolate brown colour but is white at liquid air temperature. Mercury oxide is known in two forms: yellow and red. The colour difference is due to particle size.

Both Zn and Cd form peroxides,  $ZnO_2$  and  $CdO_2$ , when their hydroxides are treated with  $H_2O_2$  solution. These peroxides are less stable. Hg does not form peroxide.

(c) Action of acids: Both zinc and cadmium dissolve in dilute hydrochloric acid and sulphuric acid with evolution of hydrogen but mercury remains unattacked.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$
  
 $Cd + 2HCl \longrightarrow CdCl_2 + H_2$   
 $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$   
 $Cd + H_2SO_4 \longrightarrow CdSO_4 + H_2$ 

Zinc and cadmium dissolve in dilute and concentrated nitric acid forming N<sub>2</sub>O, NO, NO<sub>2</sub> or NH<sub>3</sub> depending on the concentration of the acid. However, Hg with dilute HNO<sub>3</sub> forms mercurous nitrate and nitric oxide and with concentrated nitric acid it forms mercuric nitrate and nitrogen dioxide.

$$6$$
Hg +  $8$ HNO $_3$  (dil.)  $\longrightarrow 3$ Hg $_2$ (NO $_3$ ) $_2$  +  $2$ NO +  $4$ H $_2$ O  
Hg +  $4$ HNO $_3$  (conc.)  $\longrightarrow$ Hg(NO $_3$ ) $_2$  +  $2$ NO $_2$  +  $2$ H $_2$ O

Hot concentrated sulphuric acid dissolves all the metals with the evolution of sulphur dioxide.

$$M + 2H_2SO_4 \longrightarrow MSO_4 + SO_2 + 2H_2O$$
  
(Hot and conc.)

(d) Action of alkalies: Zinc dissolves in caustic alkalies with formation of zincates and evolution of hydrogen. Cadmium and mercury are not affected.

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

(e) Halides: These metals directly react with halogens.  $M + X_2 \longrightarrow MX_2$ 

The nature of the bond depends on the polarising power of the cation and the polarisability of the anion. It is observed that polarising power increases from Zn to Hg and from F to I. The covalent nature of halides increases from Zn to Hg and from F to I. All the halides except  $HgI_2$  are white solids, they have low melting points and are easily volatile.  $HgI_2$  is red but it becomes yellow on heating at  $126^{\circ}$ C. All the halides, except fluorides, form halo complexes of the type  $MX_3^-$  and  $MX_4^{2-}$  with halide ions.

(f) Sulphides: All form sulphides of the type MS, which can be precipitated by passing  $H_2S$  through their salts solutions.

The solubility products of the sulphides decrease from Zn to Hg. ZnS is soluble in dilute acids, CdS is soluble in concentrated acids but HgS is insoluble even in concentrated acids. HgS is soluble in aqua-regia.

**(g) Oxysalts:** The sulphates, nitrates, acetates and perchlorates of these metals are soluble in water. The carbonates and oxalates are insoluble. Various salts are thermally less stable. The ease of decomposition increases from zinc to mercury. Mercury salts yield mercury in some cases.

$$ZnCO_3 \longrightarrow ZnO + CO_2$$
  
 $2ZnSO_4 \longrightarrow 2ZnO + 2SO_2 + O_2$ 

$$2Zn(NO_3)_2 \longrightarrow 2ZnO + 4NO_2 + O_2$$

$$Hg_2CO_3 \longrightarrow HgO + Hg + CO_2$$

$$3HgSO_4 \longrightarrow Hg_2SO_4 + Hg + 2SO_2 + 2O_2$$

$$2Hg(NO_3)_2 \longrightarrow 2HgO + 4NO_2 + O_2$$

All the three elements form double sulphates crystallising with six molecules of water, for example, K<sub>2</sub>SO<sub>4</sub>·2nSO<sub>4</sub>·6H<sub>2</sub>O.

**(h) Complexes:** All the three elements form complexes particularly with cyanide ions, ammonia, halide ions and many other ligands. The complexes of  $Hg^{2+}$  are much more stable than  $Zn^{2+}$  and  $Cd^{2+}$ . The most common coordination number of Zn and Cd in the complexes is four. Quite a few six coordinated complexes are also known. Some examples are given below:

$$[Zn(NH_3)_4]SO_4 \qquad [Cd(NH_3)_4]SO_4$$

$$K_2Zn(CN)_4 \qquad K_2Cd(CN)_4$$

$$[Zn(en)_3]^{2+} \qquad [Cd(en)_3]^{2+}$$

$$(en = ethylene diamine)$$

The common coordination numbers of mercury are 2 and 4. For example, Hg(NH<sub>2</sub>)Cl and K<sub>2</sub>HgI<sub>4</sub>.

(i) Alloys and amalgams: Zinc forms a number of alloys with other metals. Cadmium is used for making low melting alloys with lead, bismuth and tin. Mercury forms a series of combinations with other metals known as amalgams.

# 14.21 ZINC

**Occurrence:** Zinc is usually found in the combined state although traces of the metal in the native state have been reported from Melbourne (Australia). Its chief ores are:

- 1. Zinc blende, ZnS. It is found in Burma, Belgium, Silesia and Oklahoma.
  - 2. Calamine or zincspar, ZnCO<sub>3</sub>
  - 3. Zincite, ZnO
  - 4. Willemite, Zn<sub>2</sub>SiO<sub>4</sub>

Traces of zinc in the form of organo-metallic compounds have been reported in the animal cells and in snake-poison. In India, zinc is mainly found at Zawar in Rajasthan.

**Extraction:** Zinc is extracted from its ores by two methods:

- 1. Reduction process
- 2. Electrolytic process.

#### 1. Reduction Process

It involves the following steps:

- (i) Concentration: When zinc blende is used, the powdered ore is concentrated by froth floatation process. In the case of calamine ore, the concentration is done by gravity process. If the ore contains iron oxide, the latter is removed by magnetic separation.
- (ii) Roasting: The concentrated ore is heated in excess of oxygen at about 900°C. Zinc sulphide is oxidised to zinc oxide. If some of the ore is oxidised to zinc sulphate, it also decomposes at 900°C into ZnO.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$
  
 $ZnS + 2O_2 \longrightarrow ZnSO_4$   
 $2ZnSO_4 \longrightarrow 2ZnO + 2SO_2 + O_2$ 

When the ore is calamine, it shall decompose into oxide with evolution of carbon dioxide.

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

For roasting, a reverberatory furnace may be used.

(iii) Reduction: The principal reaction that takes place during reduction is the conversion of the oxide into the metal with the help of carbon.

$$ZnO + C \longrightarrow Zn + CO$$

There are different types of reducing furnaces for the reduction of the oxide. All make use of the same principle but differ only in the details of construction and method by which the metal is separated.

(a) Belgian process: It is an old process. The roasted ore is heated with coke to about 1100°C in a small fireclay retorts. The heating is often done by producer gas. Each retort

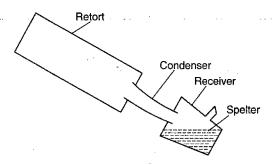


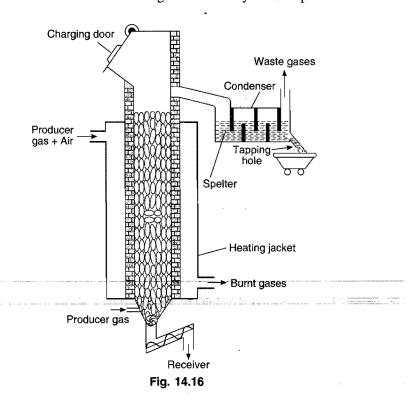
Fig. 14.15

is filled with a mixture of 2 parts ore and one part coke. The retorts are about 1.5 metre long and 25 cm in diameter. Each retort is circular or elliptical in shape and closed at one end. The mouth of each retort is provided with an earthenware condenser. The temperature is raised to about 1100°C, the CO formed during the process burns at the mouth of the retorts and when the colour of the flame changes from blue to greenish white, the condensers are fitted there on. These condensers are cooled by air and the metal condenses in these partly as a fused metal (spelter) and partly as a powder (zinc dust).

There are number of such retorts which are arranged in three or four rows one above the other.

**(b) Vertical retorts process :** This is a continuous process and is largely used these days. It is economical also.

In this process the vertical retorts of about 7.5 metre height are used. Each is connected with an arrangement for continuous



feeding of roasted ore and powdered coke. Retorts are made of highly refractory silicon carbide bricks capable of withstanding high temperature 1300°C. The retorts are heated externally by producer gas. There is an extension at the bottom through which ash can be removed. The open end of the retort is connected with condensers. Zinc vapour and carbon monoxide pass into the condensers when zinc liquefies. Molten zinc is periodically taped off from the condensers and carbon monoxide is used as fuel for heating the furnace.

(iv) Purification: The zinc obtained above is impure containing 97.8% zinc and rest impurities of lead, iron, cadmium, arsenic, etc. This impure zinc is known as spelter. This is put to further purification by distillation. The distillation is carried around 950–1000°C when only zinc (b. pt. 907°C) and cadmium (b. pt. 767°C) distil over. From this sample, cadmium is removed at 800°C.

The impure zinc can also be purified electrolytically. The impure metal is made anode and cathode consists of sheets of pure aluminium. A solution of zinc sulphate acts as an electrolyte. Zinc dissolves from anode and deposits on cathode when electric current is passed. Zinc is scraped off from the aluminium sheets.

## 2. Electrolytic Process

This method is gradually replacing the reduction process. The roasted ore is dissolved in dilute sulphuric acid and the solution is filtered. The solution is freed from iron, aluminium, silica, etc., by treatment with calcium hydroxide. Copper and cadmium are removed by precipitation with zinc dust at 75°C.

$$FeSO_4 + Ca(OH)_2 \longrightarrow Fe(OH)_2 + CaSO_4$$

$$CdSO_4 + Zn \longrightarrow Cd + ZnSO_4$$

$$CuSO_4 + Zn \longrightarrow Cu + ZnSO_4$$

The filtered solution is subjected to electrolysis by using a sheet of pure aluminium as cathode and pure lead plate as anode. The zinc is removed from cathode by melting. The zinc obtained is 99.95% pure.

Granulated zinc is made by melting the metal in a crucible and pouring the drops in water. Zinc sheet is formed by heating the metal at 150°C when it becomes soft and then can be rolled into sheets.

### Properties

**Physical:** (a) It is a bluish white metal. It acquires grey colour when exposed to moist atmosphere. (b) It melts at 419.5°C and boils at 907°C. (c) It has specific gravity 7.1. (d) It is malleable and ductile. (e) It is good conductor of heat and electricity.

Chemical: (a) Action of air: It is not affected by dry air. In moist air, a protective thin film of basic carbonate is formed on its surface. When heated in air strongly, it burns forming a white smoke which settles down to soft wooly flocks of zinc oxide called the *philosopher's wool* or *pompholyx*.

$$2Zn + O_2 \longrightarrow 2ZnO$$

(b) Action of water: Pure zinc is not affected by water. The commercial zinc decomposes boiling water. At red heat, the metal decomposes steam evolving hydrogen.

$$Zn + H_2O \longrightarrow ZnO + H_2$$

(c) Action of acids: Pure zinc is attacked slowly by acids but commercial zinc reacts readily with all acids. It dissolves in HCl (dilute and conc.) and dilute H<sub>2</sub>SO<sub>4</sub> evolving hydrogen.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$
  
 $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$ 

It dissolves in concentrated H<sub>2</sub>SO<sub>4</sub> with evolution of SO<sub>2</sub>.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + O$$

$$Zn + H_2SO_4 + O \longrightarrow ZnSO_4 + H_2O$$

$$Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + SO_2 + 2H_2O$$

Dilute nitric acid gives nitrous oxide or ammonium nitrate depending on the strength of the acid.

$$[Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4$$
  
 $2HNO_3 + 8H \longrightarrow NH_4NO_3 + 3H_2O$ 

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Dilute HNO<sub>3</sub>: Nitrous oxide is evolved.

$$[Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4$$

$$2HNO_3 + 8H \longrightarrow N_2O + 5H_2O$$

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

Conc. HNO<sub>3</sub>: Nitrogen dioxide is evolved.

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H$$
 $[HNO_3 + H \longrightarrow NO_2 + H_2O] \times 2$ 
 $Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$ 

(d) Action of alkalies: Zinc dissolves in hot caustic alkali solutions forming alkali zincate and evolving hydrogen.

$$Zn + 2KOH \longrightarrow K_2ZnO_2 + H_2$$
  
Pot. zincate

(e) Electropositive nature: Zinc displaces many metals such as lead, copper, silver, gold, etc., from their salt solutions as it is highly electropositive.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$
  
 $Zn + 2AgNO_3 \longrightarrow Zn(NO_3)_2 + 2Ag$ 

(f) Action of ammonia: Zinc decomposes ammonia at red heat.

$$3Zn + 2NH_3 \longrightarrow Zn_3N_2 + 3H_2$$

(g) Action of halogens: It reacts with halogens directly.

$$\operatorname{Zn} + X_2 \longrightarrow \operatorname{Zn} X_2$$

(h) Action of sulphur: When heated with sulphur, it forms zinc sulphide.

$$Zn + S \longrightarrow ZnS$$

#### Uses

- (i) Zinc is used in the manufacture of various important alloys such as brass, german silver, etc.
- (ii) Zinc is used in Parkes process for the extraction of silver from argentiferous lead. Zinc dust is used for the extraction of Ag and Au by cyanide process.
  - (iii) Zinc dust is used in the laboratory as a reducing agent.
  - (iv) Zinc rods are used in making electric batteries.
- (v) The most important use of zinc is for the galvanising of iron. Galvanising is a process of depositing a thin layer of zinc over the surface of iron. The zinc coating protects the iron from corrosion. The iron articles to be galvanised are first cleaned by means of a sand blast and then dipped in dilute  $H_2SO_4$  and finally washed with water. The galvanisation is done either by spraying the molten zinc or dipping in molten zinc or electrolytically.

## 14.22 COMPOUNDS OF ZINC

**Zinc oxide, ZnO:** Zinc oxide is also called zinc white or chinese white or philosopher's wool. It occurs in nature as the mineral zincite or red zinc ore.

#### Preparation

It is obtained by the combustion of zinc or by the calcination of zinc carbonate, zinc nitrate or zinc hydroxide.

$$2Zn + O_2 \longrightarrow 2ZnO$$

$$ZnCO_3 \longrightarrow ZnO + CO_2$$
  
 $2Zn(NO_3)_2 \longrightarrow 2ZnO + 4NO_2 + O_2$   
 $Zn(OH)_2 \longrightarrow ZnO + H_2O$ 

Very pure zinc oxide is prepared by mixing a solution of zinc sulphate with sodium carbonate. The basic zinc carbonate thus, precipitated on heating gives pure zinc oxide.

$$4ZnSO_4 + 4Na_2CO_3 + 3H_2O \longrightarrow ZnCO_3 \cdot 3Zn(OH)_2$$

$$ppt.$$

$$+ 4Na_2SO_4 + 3CO_2$$

$$ZnCO_3 \cdot 3Zn(OH)_2 \xrightarrow{\text{Heat}} 4ZnO + 3H_2O + CO_2$$

## Properties

(i) It is a white powder. It becomes yellow on heating and again turns white on cooling. (ii) It is very light. It is insoluble in water. It sublimes at 400°C. (iii) It is an amphoteric oxide and dissolves readily in acids forming corresponding zinc salts and alkalies forming zincates.

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$
  
 $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$   
 $ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$   
Sodium zincate

(iv) When heated in hydrogen above 400°C, it is reduced to metal.

$$ZnO + H_2 \longrightarrow Zn + H_2O$$

It is also reduced by carbon into zinc.

$$ZnO + C \longrightarrow Zn + CO$$

(v) When zinc oxide is heated with cobalt nitrate, a green mass is formed due to formation of cobalt zincate which is known as **Rinmann's green.** 

$$2\text{Co}(\text{NO}_3)_2 \longrightarrow 2\text{CoO} + 2\text{NO}_2 + \text{O}_2$$
  
 $\text{ZnO} + \text{CoO} \longrightarrow \text{CoZnO}_2 \text{ or CoO·ZnO}$ 

## Uses

- (i) Zinc oxide is used as a white pigment (paint). No doubt its covering power is less than white lead but it is superior because it is not blackened in atmosphere of hydrogen sulphide. It can be used both as oil and water paint.
- (ii) It is used to prepare Rinmann's green which is employed as a green pigment.
- (iii) It finds use as a catalyst along with Cr<sub>2</sub>O<sub>3</sub> in the manufacture of methyl alcohol from water gas.
- (iv) It is used as a filler for soft rubber and as an absorbent in surgical dressing.
- (v) It is also used as zinc ointment in medicine and as a glaze in ceramics.
  - (vi) It is used for cosmetic powders and creams.

## Zinc Chloride, ZnCl<sub>2</sub>·2H<sub>2</sub>O

### Preparation

It is obtained by treating zinc oxide or zinc carbonate or zinc hydroxide with dilute hydrochloric acid. The solution on concentration and cooling gives hydrated zinc chloride crystals, ZnCl<sub>2</sub>·2H<sub>2</sub>O.

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$
  
 $ZnCO_3 + 2HCl \longrightarrow ZnCl_2 + CO_2 + H_2O$   
 $Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + 2H_2O$ 

Anhydrous zinc chloride cannot be obtained by heating crystals of hydrated zinc chloride as hydrolysis occurs and basic chloride (zinc hydroxy chloride) is formed which on further heating gives zinc oxide.

$$ZnCl_2 \cdot 2H_2O \longrightarrow Zn(OH)Cl + HCl + H_2O$$
  
 $Zn(OH)Cl \longrightarrow ZnO + HCl$ 

The anhydrous zinc chloride is obtained by heating zinc in the atmosphere of dry chlorine or dry HCl gas.

$$Zn + Cl_2 \longrightarrow ZnCl_2$$
  
 $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$ 

This can also be formed by distilling zinc pewder with mercuric chloride.

$$Zn + HgCl_2 \longrightarrow ZnCl_2 + Hg$$

## Properties

(a) Anhydrous zinc chloride is a white solid, deliquescent and soluble in water. It melts at 660°C and boils at 730°C. (b) Hydrated zinc chloride on heating forms zinc hydroxy chloride or zinc oxychloride.

$$ZnCl_2 \cdot 2H_2O \longrightarrow Zn(OH)Cl + HCl + H_2O$$
  
 $2ZnCl_2 \cdot 2H_2O \longrightarrow Zn_2OCl_2 + 2HCl + 3H_2O$   
Zinc oxychloride

(c) When H<sub>2</sub>S is passed through the solution, a white precipitate of zinc sulphide, is formed.

$$ZnCl_2 + H_2S \longrightarrow ZnS + 2HCl$$

(d) When NaOH is added, a white precipitate of zinc hydroxide appears which dissolves in excess of sodium hydroxide forming sodium zincate.

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$$
  
 $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$ 

(e) On adding NH<sub>4</sub>OH solution, a white precipitate of zinc hydroxide appears which dissolves in excess of ammonia forming a complex salt.

$$ZnCl_2 + 2NH_4OH \longrightarrow Zn(OH)_2 + 2NH_4Cl \xrightarrow{3}$$
 $Zn(OH)_2 + 2NH_4OH + 2NH_4Cl \longrightarrow [Zn(NH_3)_4]Cl_2 + 4H_2O$ 
Tetrammine zinc chloride

Transition Elements or d-block Elements and f-block Elements

(f) When the solution of zinc chloride is treated with a solution of sodium carbonate, a white precipitate of basic zinc carbonate is formed.

But when a solution of sodium bicarbonate is used, a white precipitate of normal zinc carbonate is formed.

$$ZnCl_2 + 2NaHCO_3 \longrightarrow ZnCO_3 + 2NaCl + H_2O + CO_2$$

(g) Anhydrous zinc chloride absorbs ammonia gas and forms an addition compound.

$$ZnCl_2 + 4NH_3 \longrightarrow ZnCl_2 \cdot 4NH_3$$

- (h) Its syrupy solution dissolves cellulose.
- (i) Its syrupy solution when mixed with zinc oxide, ZnO, sets to a hard mass forming an oxychloride, ZnCl<sub>2</sub>·3ZnO.

#### **■** Uses

- (i) The concentrated solution of zinc chloride is used for impregnating timber to prevent its destruction from the action of micro-organisms.
- (ii) The mixture of syrupy zinc chloride solution and zinc oxide is used for dental filling.
  - (iii) It is used as dehydrating agent.
- (iv) Being acidic in aqueous solution, it is used for cleaning the surface of metals before soldering.
- (v) It is employed in making parchment paper; vulcanised fibre, cold water glues and adhesives. It is also used in the manufacture of dry cells.

# Zinc Sulphate (White vitriol), ZnSO4.7H2O

## Preparation

It is prepared by reacting zinc with dilute sulphuric acid. It can also be prepared by dissolving zinc oxide or carbonate in dilute sulphuric acid. The solution on concentration and crystallisation below 39°C gives colourless crystals of zinc sulphate,  $ZnSO_4 \cdot 7H_2O$ .

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
  
 $ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$   
 $ZnCO_3 + H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$ 

## Properties

- (a) It is a colourless, crystalline solid. It is an efflorescent substance. It is freely soluble in water.
  - (b) On heating, the following changes occur.

$$\begin{array}{c} ZnSO_4 \cdot 7H_2O \xrightarrow{Above \ 39^{\circ}C} ZnSO_4 \cdot 6H_2O \xrightarrow{Above \ 70^{\circ}C} ZnSO_4 \cdot H_2O \\ & Above \ 280^{\circ}C \bigcup \\ O_2 + SO_2 + ZnO \xrightarrow{(Anhydrous)} ZnSO_4 \end{array}$$

$$ZnSO_4 \xrightarrow{800^{\circ}C} ZnO + SO_3$$

$$\downarrow \qquad \qquad \downarrow \qquad \qquad \downarrow \qquad \qquad SO_2 + \frac{1}{2}O_2$$

(c) When sodium hydroxide is added to the solution of zinc sulphate, a white precipitate of zinc hydroxide appears which dissolves in excess of NaOH forming sodium zincate.

$$ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2 + Na_2SO_4$$
  
 $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$ 

(d) When sodium carbonate solution is added to the solution of zinc sulphate, a white precipitate of basic zinc carbonate is formed.

$$4ZnSO_4 + 4Na_2CO_3 + 3H_2O \longrightarrow ZnCO_3 \cdot 3Zn(OH)_2 + 4Na_2SO_4 + 3CO_2$$

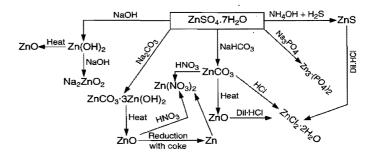
However, when the solution of sodium bicarbonate is added, normal zinc carbonate is formed.

$$ZnSO_4 + 2NaHCO_3 \longrightarrow ZnCO_3 + Na_2SO_4 + H_2O + CO_2$$

(e) With alkali metal sulphates and  $(NH_4)_2SO_4$ , it forms double sulphates such as  $K_2SO_4$ ·ZnSO<sub>4</sub>·6H<sub>2</sub>O.

#### Uses

- (i) A dilute solution of zinc sulphate is used as eye lotion.
- (ii) It is used for the preparation of lithopone (ZnS + BaSO<sub>4</sub>), a popular white paint.
  - (iii) It is employed as a mordant in dyeing and calicoprinting.
- (iv) The solution of zinc sulphate is used for zinc plating and in the electrolytic refining of zinc.
- (v) Zinc sulphate is used as a starting material for the preparation of other zinc compounds.



## 14.23 MERCURY

Occurrence: Mercury ores are rare. It occurs in small quantities in the native state. Cinnabar, HgS, is the most important ore and is found in Spain and Italy and small quantities in Russia, United States of America, Mexico, China and Japan.

**Extraction:** The extraction of mercury from cinnabar ore is comparatively simple and consists mainly the roasting and distillation. The extraction involves the following steps:

- (i) Crushing and concentration: The ore is crushed and finely powdered in ball mills and concentrated by froth floatation process.
- (ii) Combined roasting and distillation: There are two principal processes available which differ only in the type of furnace used.
- (a) Idrian furnace used in Almaden (Spain). This is the old process.
  - (b) Shaft furnace—This is the modern continuous process.

#### (a) Idrian Furnace

The concentrated ore is taken on the perforated arches and heated by the flame (Fig. 14.17).

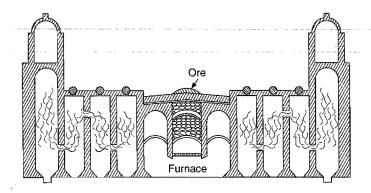


Fig. 14.17

The mercuric sulphide undergoes oxidation with evolution of sulphur dioxide. The mercuric oxide thus formed decomposes at 300°C to give mercury vapours.

$$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$$
  
 $2HgO \longrightarrow 2Hg + O_2$ 

The vapours of mercury are condensed in a series of condensers on either side of the furnace. Most of the metal collects in the first three condensers and in the last condenser, the condensation is assisted by water spray or wet straw dust.

#### (b) The Shaft Furnace

The ore chamber is cylindrical, standing on a hexagonal base. The concentrated ore, mixed with charcoal is added to the furnace by a cup and cone arrangement. There are three fire places communicating with the chamber on the alternate sides of the hexagon. The furnace is heated to a red heat. Air is admitted along with the flames. Gases with mercury vapours, pass through iron pipes into watercooled condensers. There is an opening in the bottom of the furnace for the removal of spent ore.

The ore is sometimes mixed with lime before roasting. This helps in the oxidation of mercuric sulphide.

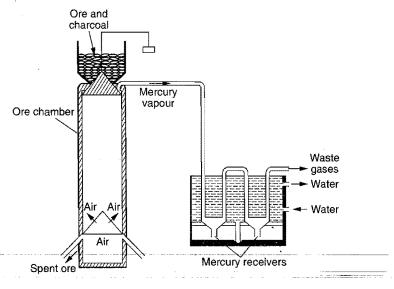


Fig. 14.18

$$HgS + CaO \longrightarrow HgO + CaS$$
  
 $2HgO \longrightarrow 2Hg + O_2$ 

- (iii) Purification: Commercial mercury is usually contaminated with other elements such as zinc, copper, lead, etc. It may be purified by the following methods.
- (a) To remove suspended particles mercury is squeezed through linen or chamois leather.
- (b) The more basic metals such as lead and zinc, which are easily oxidised, are removed as scum of their oxides when dust free air is passed through mercury at 150°C.
- (c) The mercury is dropped in a long tube filled with dilute nitric acid (about 5%). The base metals dissolve in dilute nitric acid as their nitrates.
  - (d) Further purification is done by vacuum distillation.

#### Properties

Mercury is a silvery white heavy liquid (Sp. gr. 13.6). It solidifies at -38.9°C to a white lustrous mass and boils at 357°C. Its vapour is very poisonous. It has a high surface tension and forms spherical drops easily.

It is not affected by air or oxygen at ordinary temperature but when heated at 340°C in air, it slowly combines with oxygen forming a red scum of HgO on the surface. When exposed to ozone, it gets superficially oxidised and loses its meniscus and sticks to the glass.

When rubbed with sulphur, it forms mercuric sulphide, HgS. It vigorously combines with chlorine, slowly with bromine and iodine.

It is not attacked by water and alkalies. Hydrochloric acid, dilute sulphuric acid and very dilute nitric acid have no action on mercury. Hot concentrated sulphuric acid, dilute and concentrated nitric acid dissolve it.

With conc. H<sub>2</sub>SO<sub>4</sub>:

$$H_2SO_4 \longrightarrow H_2O + SO_2 + O$$

$$Hg + H_2SO_4 + O \longrightarrow HgSO_4 + H_2O$$

$$Hg + 2H_2SO_4 \longrightarrow HgSO_4 + SO_2 + 2H_2O$$

With dilute HNO3:

$$2HNO_{3} \longrightarrow H_{2}O + 2NO + 3[O]$$

$$[2Hg + O \longrightarrow Hg_{2}O] \times 3$$

$$[Hg_{2}O + 2HNO_{3} \longrightarrow Hg_{2}(NO_{3})_{2} + H_{2}O] \times 3$$

$$6Hg + 8HNO_{3} \longrightarrow 3Hg_{2}(NO_{3})_{2} + 2NO + 4H_{2}O$$

With conc. HNO<sub>3</sub>:

$$2HNO_{3} \longrightarrow H_{2}O + 2NO_{2} + O$$

$$Hg + 2HNO_{3} + O \longrightarrow Hg(NO_{3})_{2} + H_{2}O$$

$$Hg + 4HNO_3 \longrightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

Mercury is acted upon by HI on account of the formation of a complex ion  $[HgI_4]^{2-}$ .

$$Hg + 2HI \longrightarrow HgI_2 + H_2$$
  
 $HgI_2 + 2HI \longrightarrow H_2HgI_4$ 

Mercury dissolves many metals and the combinations are called amalgams. Gold, silver, tin, lead, magnesium, copper, sodium, potassium, etc., when rubbed with mercury form amalgams. Iron, cobalt and nickel do not form amalgams directly.

#### ■ Uses

Mercury is used (i) in thermometers, barometers, and other physical apparatus (ii) in the extraction of Ag and Au (iii) in the manufacture of caustic soda by the electrolytic process (iv) in the form of amalgams as reducing agents. (v) in mercury vapour lamps which give out bluish light. (vi) in making dental plastic (vii) in the manufacture of vermilon (HgS).

#### 14.24 COMPOUNDS OF MERCURY

#### Mercurous Chloride, Hg<sub>2</sub>Cl<sub>2</sub> (Calomel)

#### Preparation

(i) By adding dilute hydrochloric acid or sodium chloride solution to a mercurous salt solution, usually mercurous nitrate, a white precipitate of mercurous chloride is formed.

$$Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 + 2HNO_3$$
  
 $Hg_2(NO_3)_2 + 2NaCl \longrightarrow Hg_2Cl_2 + 2NaNO_3$ 

(ii) Metallic mercury is boiled with concentrated sulphuric acid and the product, mercuric sulphate is then ground thoroughly with common salt and metallic mercury. The mixture is sublimed to separate  $Hg_2Cl_2$ .

$$\begin{aligned} & \text{Hg} + 2\text{H}_2\text{SO}_4 & \longrightarrow \text{HgSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O} \\ & \text{HgSO}_4 + 2\text{NaCl} + \text{Hg} & \longrightarrow \text{Hg}_2\text{Cl}_2 + \text{Na}_2\text{SO}_4 \end{aligned}$$

(iii) It can be obtained by passing sulphur dioxide through the solution of mercuric chloride.

$$2HgCl_2 + 2H_2O + SO_2 \longrightarrow Hg_2Cl_2 + H_2SO_4 + 2HCl$$

(iv) Mercurous chloride for medicinal purposes is prepared by heating a mixture of mercuric chloride and mercury in an iron pot. The sublimate is ground and boiled with water to remove traces of mercuric chloride.

$$HgCl_2 + Hg \longrightarrow Hg_2Cl_2$$

#### Properties

- (i) It is an amorphous, tasteless, odourless white powder. It is sparingly soluble in water. It sublimes at 373°C. It is non-poisonous.
- (ii) It dissolves in hot concentrated nitric acid forming mercuric chloride and mercuric nitrate.

$$3Hg_2Cl_2 + 8HNO_3 \longrightarrow 3HgCl_2 + 3Hg(NO_3)_2 + 4H_2O + 2NO_3$$

(iii) It dissolves in chlorine water, aqua-regia or a mixture of KClO<sub>3</sub> and concentrated HCl.

$$Hg_2Cl_2 + 2Cl \longrightarrow 2HgCl_2$$

(iv) On heating, it decomposes into mercuric chloride and mercury.

$$Hg_2Cl_2 \longrightarrow Hg + HgCl_2$$

(v) When caustic soda solution is added in excess to a mercurous chloride solution in HCl, a black precipitate of mercurous oxide is formed which is decomposed under the action of light.

$$Hg_2Cl_2 + 2NaOH \longrightarrow Hg_2O + 2NaCl + H_2O$$
  
 $Hg_2O \longrightarrow HgO + Hg$ 

(vi) It turns black when treated with ammonium hydroxide. The black substance is a mixture of mercury and mercuric amino chloride.

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow Hg \stackrel{NH_2}{\longleftarrow} + Hg + NH_4Cl + 2H_2O$$

(vii) It is reduced to mercury with stannous chloride.

$$SnCl_2 + Hg_2Cl_2 \longrightarrow 2Hg + SnCl_4$$

(viii) It absorbs ammonia gas and forms an addition compound.

$$Hg_2Cl_2 + 2NH_3 \longrightarrow Hg_2Cl_2 \cdot 2NH_3$$

#### ■ Uses

- (i) As a purgative in medicine.
- (ii) For making calomel electrodes.

### Mercuric Chloride (Corrosive sublimate), HgCl<sub>2</sub>

#### Preparation

(i) The compound was formerly prepared on commercial

scale by heating a mixture of mercuric sulphate with common salt. A little manganese dioxide was added to prevent the formation of any mercurous chloride. Mercuric chloride sublimes off and condenses on the cooler parts of the vessel.

$$HgSO_4 + 2NaCl \longrightarrow HgCl_2 + Na_2SO_4$$

(ii) The compound is now commercially made by heating the metal in a current of chlorine.

$$Hg + Cl_2 \longrightarrow HgCl_2$$

(iii) It can be prepared by dissolving mercuric oxide in hydrochloric acid.

$$HgO + 2HCl \longrightarrow HgCl_2 + H_2O$$

(iv) It can also be prepared by dissolving Hg or Hg<sub>2</sub>Cl<sub>2</sub> in aqua-regia.

$$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl$$

$$Hg + 2Cl \longrightarrow HgCl_2$$

$$Hg_2Cl_2 + 2Cl \longrightarrow 2HgCl_2$$

#### Properties

- (i) It is a white crystalline compound. It is less soluble in cold water but more soluble in hot water. It behaves like a covalent compound as it is soluble in organic solvents and very slightly ionised in water.
- (ii) It has corrosive action. It is highly poisonous. It sublimes on heating. It is, therefore, known as corrosive sublimate.
- (iii) It is reduced by stannous chloride first into mercurous chloride (white) and then into mercury (black).

$$\begin{array}{c} 2 \text{HgCl}_2 + \text{SnCl}_2 \longrightarrow \text{Hg}_2 \text{Cl}_2 + \text{SnCl}_4 \\ \text{White} \\ \text{Hg}_2 \text{Cl}_2 + \text{SnCl}_2 \longrightarrow 2 \text{Hg} + \text{SnCl}_4 \\ \text{Black} \end{array}$$

(iv) When aqueous ammonia is added to the solution of mercuric chloride, a white precipitate of mercuric amino chloride is formed.

$$HgCl_2 + 2NH_4OH \longrightarrow Hg \begin{cases} NH_2 \\ Cl \end{cases} + NH_4Cl + 2H_2O$$

(v) Mercuric chloride absorbs gaseous ammonia and forms a complex salt.

$$HgCl_2 + 2NH_3 \longrightarrow Hg(NH_3)_2Cl_2$$
Mercuric diamine chloride

(vi) When H<sub>2</sub>S is passed through its solution, it forms a black precipitate of mercuric sulphide.

$$HgCl_2 + H_2S \longrightarrow HgS + 2HCl$$

(vii) When heated with sodium carbonate or sodium hydroxide in solution, a yellow precipitate of mercuric oxide is formed.

$$HgCl_2 + Na_2CO_3 \longrightarrow HgO + 2NaCl + CO_2$$
  
 $HgCl_2 + 2NaOH \longrightarrow HgO + 2NaCl + H_2O$ 

(viii) Potassium iodide forms a scarlet precipitate of mercuric iodide when added to  $HgCl_2$  solution. The precipitate of mercuric iodide dissolves in excess of potassium iodide forming a complex,  $K_2HgI_4$ .

$$HgCl_2 + 2KI \longrightarrow 2KCl + HgI_2$$
  
 $HgI_2 + 2KI \longrightarrow K_2HgI_4$ 

The alkaline solution of this complex is known as Nessler's reagent. This reagent is used for testing ammonia. When ammonia or ammonium salts are present, the brown precipitate is obtained. This precipitate is said to be the iodide of Millon's base, probably having the composition:

$$\begin{bmatrix} IHg & H \\ IHg & N \end{bmatrix}^{+} I^{-} \text{ or } \begin{bmatrix} Hg & H \\ O & N \end{bmatrix} I \cdot 2H_{2}O$$

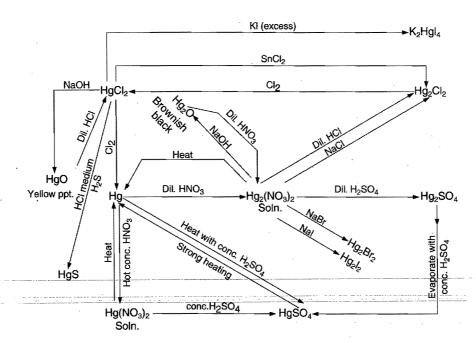
$$(B)$$

The formation of the iodide of Millon's base can be explained as follows:

#### ■ Uses

(i) It is highly poisonous and hence used as germicide. It is used as an antiseptic. A very dilute solution is employed for the sterilization of surgical instruments. (ii) For the preparation of Nessler's reagent which is used for the test of ammonia and ammonium compounds. (iii) It is used in dry cells and as a wood preservative.

**Note:** It is a strong poison, its antidote being the white of an egg which eliminates it from the system in the form of a coagulated mass.



### 14.25 PHOTOGRAPHY

The art of obtaining an exact impression of an object on a plate or paper by a chemical reaction initiated by light is called photography. It is based on the nature of silver halides. Except AgF, the silver halides are photosensitive. Silver halides, particularly silver bromide, undergo decomposition in light and turn black due to formation of free silver.

$$2AgBr \xrightarrow{Light} 2Ag + Br_2$$

The entire process of photography involves the following steps:

### 1. Preparation of photographic plate or film

An emulsion of silver bromide is prepared in a dark room by mixing silver nitrate solution with ammonium bromide solution containing gelatine with constant stirring.

$$NH_4Br + AgNO_3 \longrightarrow AgBr + NH_4NO_3$$

The emulsion is allowed to stand at about 45°C for some time so that the particles of silver bromide may grow in size. This treatment is termed as the *ripening of emulsion*. The emulsion is now cooled in ice as to solidify. It is washed with water in order to make it free from ammonium nitrate. It is warmed to melt it again.

The melted emulsion is applied uniformly on a celluloid film or smooth glass plate. Whole of this operation should be done in a dark and dust-free room.

#### 2. Exposure

The light-sensitive film or plate is loaded in a camera which is focussed on the object to be photographed. When the shutter of the camera is opened for a few seconds, the light from the object through the lens falls on the film or plate. The silver bromide is affected by light and gets activated. This is not a visible change but is called formation of *latent image*.

The light reduces silver bromide. The effect produced on the film or plate is directly proportional to the intensity of light.

$$2AgBr \rightleftharpoons 2Ag + Br_2$$

Bromine is absorbed by gelatine and helps in the decomposition of silver bromide. According to one theory (Gurney-Mott theory), the following sequence of events occur:

- (i) An incoming quantum of light hv kicks an electron out of Br to form Br and  $e^-$ .
- (ii) The electron wanders through the crystal of AgBr and eventually gets trapped at a surface defect.
- (iii) An interstitial  $Ag^+$ , such as is commonly found in AgBr, diffuses to the trap site where the  $Ag^+$  and the trapped  $e^-$  combine to give Ag.
- (iv) A second quantum of light energy hv comes along and ejects a second electron which migrates to Ag and converts it into Ag<sup>-</sup>.
- (v) A second interstitial  $Ag^+$  subsequently diffuses over and combines.

$$Ag^+ + Ag^- \longrightarrow Ag_2$$

(vi) The process repeats until a clump of about 50 silver atoms is built up. The AgBr grain is now "activated".

#### 3. Developing

The treatment of the exposed photographic film with reducing agents is called developing of the film. The chemicals used for developing as reducing agents are called developers. A developer is usually a weak reducing agent such as potassium ferrous oxalate or an alkaline solution of pyrogallol or an alkaline solution of quinol, etc.

The exposed film or plate is kept in a solution of a developer for some time. The parts activated by light are reduced to deposit more of black silver.

$$2 Ag Br + C_6 H_4 (OH)_2 \xrightarrow{} 2 Ag + 2 H Br + C_6 H_4 O_2$$

$$\underset{Quinone}{\text{Quinone}}$$

The developer does not affect those parts of the photographic film or plate which are not activated by light. On the developed film or plate the shades of the object are reversed, *i.e.*, the bright parts of the object appear dark and the dark parts appear bright. The plate or film is, therefore, called a *negative*. This operation is carried out in dark.

### 4. Fixing

In order to make the image permanent, it is necessary to remove the unreduced silver bromide from the surface of the developed film. This operation is called *fixing of image*. Fixing is done by dipping the developed film or plate in sodium thiosulphate (hypo) solution. The hypo solution dissolves the unreduced silver bromide by forming a complex.

This operation is also done in dark.

The plate is now thoroughly washed with water and dried. It can now be taken out of the dark room into light.

#### 羅 5. Printing

To get a positive image, the whole process is repeated. The Printing Out Paper (POP) or bromide paper is used. The POP has got a coating of silver bromide emulsion. The negative is placed over POP and then exposed to light for a fraction of a second. A negative of the *negative plate* or positive with respect to the actual object is obtained on the print paper. The print paper is then subjected to developing and fixing as usual. The positive print has shades exactly similar to those of the object.

#### 6. Toning

It is a technique by which different shades can be given to the printed photograph with the help of chemicals. The printed photograph obtained is black and white. This photograph is dipped in a solution containing the salt solution of either gold or platinum or selenium, etc. The dark silver particles are replaced by another metal. Thus, gold salt gives golden shade and platinum salt makes the shade bright grey.

$$\begin{array}{c} AuCl_3 + 3Ag \longrightarrow Au + 3AgCl \\ \hline \\ PtCl_4 + 4Ag \longrightarrow Pt + 4AgCl \\ \hline \\ \\ Steel \ grey \end{array}$$

The various steps involved in photography are shown in Fig. 14.19.

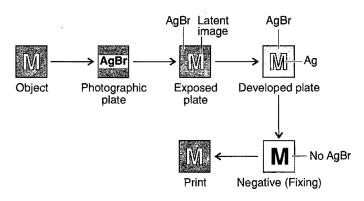


Fig. 14.19

### 14.26 f-Block Elements

28 elements from atomic number 58 to 71 (14 elements) and from atomic number 90 to 103 (14 elements) have been arranged in two horizontal rows below the periodic table. These elements are collectively called f-block elements as the last or differentiating electron in the atoms of these elements is accommodated on one of the seven f-orbitals of the antepenultimate (next to the penultimate) energy shell. These elements have also been called **inner transition elements** because the ante-penultimate energy shell, *i.e.*, (n-2)f-orbitals, lie comparatively deep within the kernel (being inner to the penultimate shell).

f-block consists of two series of elements known as Lanthanides or Lanthanons and Actinides or Actinons. The lanthanide series follows lanthanum (At. No. 57), a member of 5d-series. Similarly, actinide series comes after actinium (At. No. 89), a member of 6d-series. The 14 members of lanthanide series have been placed along with lanthanum in the third group and sixth period and similarly 14 members of the actinide series have been placed with actinium in the third group and seventh period. The justification for assigning one place to these elements has been given on the basis of their similar properties. The properties are so similar that the fifteen elements from La to Lu can be considered as equivalent to one element. The same explanation can be given in the case of actinides. In case, these elements are assigned different positions in order of their increasing atomic numbers, the symmetry of the whole arrangement would be disrupted. Due to this reason, the two series of elements, i.e., lanthanides and actinides are placed at the bottom of the periodic table and constitute one block of elements, i.e., f-block. The general electronic configuration of the f-block elements is:

$$(n-2)f^{1-14}(n-1)d^{0,1}ns^2$$
 or  $4f^{1-14}5d^{0,1}6s^2$ 

(a) 4f-series (Lanthanides): There are fourteen elements from cerium (At. No. 58) to lutetium (At. No. 71) in this series. 4f-orbitals are gradually filled up. In the past, these

elements were called **rare earths.** This name is not appropriate because many of the elements are not particularly rare. Promethium is artificial radioactive element.

**(b) 5**f-series (**Actinides**): There are fourteen elements from thorium (At. No. 90) to lawrencium (At. No. 103) in this series. 5f-orbitals are gradually filled up. The members of actinium are radioactive and majority of them are not found in nature. The elements from atomic number of 93 onwards are called transuranic elements and have been discovered by synthetic methods, *i.e.*, these are man made elements.

## 14.27

# GENERAL CHARACTERISTICS OF LANTHANIDES

The general characteristics are similar to transition metals, *i.e.*, *d*-block elements.

#### **1. Electronic configuration**

The energies of 5d- and 4f-orbitals are nearly similar and thus their fillings show certain irregularities. The electronic configurations of the atoms of the lanthanides in their ground state are given in the following table. These are the most commonly accepted configurations.

Name of the	Symbol	Atomic number	Electronic configuration	Oxidation states
Lanthanum	La	57	$[Xe]5d^16s^2$	+3
Cerium	Ce	58	$[Xe]4f^15d^16s^2$	+3, +4
Praseodymium	Pr	59	$[Xe]4f^36s^2$	+3, (+4)
Neodymium	Nd	60	$[Xe]4f^46s^2$	(+2), +3
Promethium	Pm	61	$[Xe]4f^56s^2$	(+2), +3
Samarium	Sm	62	$[Xe]4f^66s^2$	(+2), +3
Europium	Eu	63	$[Xe]4f^76s^2$	+2, +3
Gadolinium	Gd	64	$[Xe]4f^{7}5d^{1}6s^{2}$	+3
Terbium	Tb	65	$[Xe]4f^96s^2$	+3, +4
Dysprosium	Dy	66	$[Xe]4f^{10}6s^2$	+3, (+4)
Holmium	Но	67	$[Xe]4f^{11}6s^2$	+3
Erbium	Er	68	$[Xe]4f^{12}6s^2$	+3
Thulium	Tm	69	$[Xe]4f^{13}6s^2$	(+2), +3
Ytterbium	Yb	70	$[Xe]4f^{14}6s^2$	+2, +3
Lutetium	Lu	71	$[Xe]4f^{14}5d^{1}6s^{2}$	+3

The electronic configuration of lanthanum is  $[Xe]5d^16s^2$ . It is expected that 14 elements from cerium to lutetium would be formed by adding, 1, 2, 3,...14 electrons into the 4f level. However, it is energetically favourable to move the single electron on 5d into the 4f level in most of the elements but not in the cases of Ce, Gd and Lu. In Gd and Lu besides  $5d^1$ , the 4f-orbitals are half filled or fully filled. This gives extra stability to the core. The extra stability of half filled and fully filled f-orbitals is also seen in Eu( $4f^76s^2$ ) and Yb( $4f^{14}6s^2$ ).

#### 2. Oxidation states

The common stable oxidation state of all the lanthanides is +3. The oxidation states of +2 and +4 are also exhibited by some of the elements. These oxidation states are only stable in those cases where stable  $4f^0$ ,  $4f^7$  or  $4f^{14}$  configurations are achieved.

For example,  $Ce^{4+}(4f^0)$ ,  $Tb^{4+}(4f^7)$ ,  $Eu^{2+}(4f^7)$ ,  $Yb^{2+}(4f^{14})$  are stable. The oxidation states shown in parantheses in the above table are less stable. +2 or +4 oxidation states tend to revert to the more stable oxidation state of +3 by loss or gain of an electron  $Sm^{2+}$ ,  $Eu^{2+}$  and  $Yb^{2+}$  ions are thus good reducing agents in solutions while  $Ce^{4+}$ ,  $Tb^{4+}$  ions, etc., are good oxidising agents. The compounds of lanthanides are mainly ionic in nature.

# 3. Atomic and ionic radii(Lanthanide contraction)

In lanthanide series, there is a regular decrease in the atomic as well as ionic radii of trivalent ions  $(M^{3+})$  as the atomic number increases from cerium to lutetium. This decrease in size of atoms and ions is known as **Lanthanide contraction**. Although the atomic radii do show some irregularities but ionic radii decrease steadily from La to Lu. However, the decrease is very small. For example,

Element	Atomic radii (pm)	Ionic radii (pm) (M <sup>3+</sup> )
La	169	103
Ce	165	102
Pr	164	99
Nd	164	98.3
Pm		97
Sm	166	95.8
Eu	185	94.7
Gd	161	93.8
Tb	159	92.3
Dy	159	91.2
Но	158	90
Er	157	89
Tm	156	. 88
Yb	170	86.8
Lu	156	. 86

On moving from Ce to Lu, the decrease in atomic radii occurs from 165 to 156 pm, *i.e.*, the decrease is only 9 pm. Similarly, the decrease in ionic radii occurs from 102 (Ce<sup>3+</sup>) to 86 (Lu<sup>3+</sup>) pm, *i.e.*, the decrease is only 16 pm. Thus, for an increase of 14 in the atomic number, the decrease in atomic radii or ionic radii are very small in comparison to the elements of other groups and periods.

Cause of lanthanide contraction: As we proceed from one element to the next element in the lanthanide series, the nuclear charge, *i.e.*, atomic number increases by one unit and the addition of one electron occurs at the same time in 4f-energy shell. On account of the very diffused shapes of forbitals, the 4f electrons shield each other quite poorly from the nuclear charge. Thus, the effect of nuclear charge increase is somewhat more than the changed shielding effect. This brings the valence shell nearer to the nucleus and hence the size of atom or ion goes on decreasing as we move in the series. The sum of the successive reductions is equal to the total lanthanide contraction.

**Consequences of lanthanide contraction:** The main consequences of lanthanide contraction are the following:

- (i) Similar chemical properties: Since the change in the ionic radii in the lanthanide series is very small, their chemical properties are similar. Thus, it is very difficult to separate these elements in the pure state. However, lanthanide contraction brings some differences in properties like solubility, complex ion formation, hydration, etc. These differences help in the separation of lanthanide elements by fractional crystallisation or ion exchange methods.
- (ii) Basic strength of hydroxides: As the size of the lanthanide ions decreases from  $Ce^{3+}$  to  $Lu^{3+}$ , the covalent character of M—OH bond increases and hence the basic strength decreases. Thus,  $Ce(OH)_3$  is most basic while  $Lu(OH)_3$  is least basic.
- (iii) Similarity of second and third transition series: In vertical columns of transition elements, there is an increase in size from first member to second member as expected but from second member to third member, there is very small change in size and sometimes sizes are same. This is due to lanthanide contraction.

In each vertical column of transition elements, the elements of second and third transition series resemble each other more closely than the elements of first and second transition series on account of lanthanide contraction. The pairs of elements such as Zr-Hf, Mo-W, Nb-Ta, etc., possess almost the same properties.

#### 4. Physical properties

All the lanthanides are metals. They are soft, malleable and ductile in nature. They are not good conductors of heat and electricity. They are highly dense metals and their densities are in the range of 6.77 to 9.74 g cm<sup>-3</sup>. The densities and atomic

volumes, in general, increase with increase in atomic number. But a regular trend is not observed. They have fairly high melting points. However, no definite trend is observed.

#### 5. Ionisation energies

Lanthanides have fairly low ionisation energies.  $IE_1$  and  $IE_2$  values are quite comparable with the values of alkaline earth metals, particularly calcium. The sum of the first three ionisation energies in kJ mol<sup>-1</sup> for each element are given below. The values are low.

Due to low values of ionisation energies, lanthanides are highly electropositive in nature. These elements react with cold and hot water to liberate hydrogen. The reactions are, however, slow with cold water but fast with hot water.

The values of standard reduction potential ( $E^{\circ}$  values) increase from La to Lu.  $E^{\circ}$  values become less negative in the series. The values in volts are given.

All the lanthanides are, thus, strong **reducing agents.** The reducing power decreases from La to Lu.

#### **6.** Coloured ions

Many of the lanthanide ions are coloured in solid state as well as in solutions. The colour is due to partially filled f-orbitals which allow f-f transitions.  $M^{3+}$  ions having  $4f^{0}$ ,  $4f^{7}$  or  $4f^{14}$  configurations are colourless.

$$\left. \begin{array}{l} \text{La}^{3+}(4f^{\,0}) \\ \text{Gd}^{3+}(4f^{\,7}) \\ \text{Lu}^{3+}(4f^{\,14}) \end{array} \right\} \text{Colourless}$$

Pairs of  $M^{3+}$  ions having the same number of unpaired electrons in 4f-orbitals have the same colour.

$$\begin{array}{c} \Pr^{3+}(4f^2) \\ \operatorname{Tm}^{3+}(4f^{12}) \end{array} \text{ Green } \\ \operatorname{Sm}^{3+}(4f^{12}) \end{array} \begin{array}{c} \operatorname{Nd}^{3+}(4f^3) \\ \operatorname{Er}^{3+}(4f^{11}) \end{array} \text{ Pink } \\ \operatorname{Sm}^{3+}(4f^5) \\ \operatorname{Dy}^{3+}(4f^9) \end{array} \text{ Yellow } \\ \operatorname{Eu}^{3+}(4f^6) \\ \operatorname{Tb}^{3+}(4f^8) \end{array} \text{ Pale pink }$$

[Note: The cations namely  $Ce^{3+}(4f^1)$  and  $Yb^{3+}(4f^{13})$  are colourless inspite of the fact that these ions have one f-orbital singly occupied. These exceptions are difficult to explain.]

#### 7. Magnetic properties

Ions having unpaired electrons are paramagnetic while those having all the orbitals paired are diamagnetic. The lanthanide ions  $(M^{3+})$  except  $\operatorname{La}^{3+}(4f^0)$  and  $\operatorname{Lu}^{3+}(4f^{14})$  are paramagnetic since they contain 1, 2,...7 unpaired electrons.

#### 8. Chemical reactivity

All the lanthanides have almost similar chemical reactivity. The metals tarnish readily in air and on heating in  $O_2$  form oxides of the type  $M_2O_3$ . The one exception is cerium which forms  $CeO_2$  rather than  $Ce_2O_3$ . The oxides are ionic and basic.

The metals react with hydrogen but often require heating up to 300–400°C. The products are solids of formula  $MH_3$ . The hydrides are decomposed by water and react with  $O_2$ . The anhydrous halides,  $MX_3$ , can be made by heating the metal and halogen or by heating the metal oxide with the appropriate ammonium halide.

$$M_2O_3 + 6NH_4C1 \xrightarrow{300^{\circ}C} 2MCl_3 + 6NH_3 + 3H_2O$$

The fluorides are very insoluble. The chlorides are deliquescent and soluble. At elevated temperatures, lanthanides react with N, C, S, P, As, Sb and Bi. A wide variety of oxo salts are known. The carbonates, phosphates, chromates, oxalates, etc., are largely insoluble in water while nitrates, acetates, sulphates, etc., are soluble.

Because of their similar chemical reactivities, their separation from one another is very difficult.

#### 3 9. Complex formation

The lanthanides do not have much tendency to form complexes due to low charge density because of their large size. However, the tendency to form complexes and their stability increases with the increase of atomic number.

#### ■ Uses of Lanthanides

The metals are seldom used in pure state. As lanthanides do not differ much in their physical and chemical properties, these are mostly used in the form of alloys. Some common uses of lanthanides and their compounds are given below:

- (i) Misch metal (an alloy): Misch metal is an alloy consisting lanthanide metals (94–95%), iron (5%) and traces of sulphur, carbon, silicon, calcium and aluminium. The main lanthanide metals present are cerium (about 40%), lanthanum and neodymium (about 44%). These alloys are used for making ignition devices such as tracer bullets, shells and flints for lighters.
  - An alloy of magnesium and about 3% misch metal is used in making jet engine parts. Cerium-magnesium alloys are used in flash light powders.
- (ii) Cerium salts are used in dyeing cotton, in lead accumulators and as catalyst.

- (iii) Lanthanum oxide is used for polishing glass. Neodymium and praseodymium oxides are used for making coloured glasses for goggles. CeO<sub>2</sub> is used in gas mantles.
- (iv) Ceric sulphate is a well known oxidising agent in volumetric analysis.
- (v) Many lanthanide oxides are used as phosphorus in colour TV tubes.
- (vi) Various compounds of lanthanides are used as catalysts for hydrogenation, dehydrogenation, oxidation and petroleum cracking.
- (vii) The compounds of lanthanides are used in making magnetic and electronic devices for their paramagnetic and ferromagnetic properties.
- (viii) Neodymium oxide dissolved in selenium oxy-chloride is used these days as a powerful liquid laser.

# 14.28 GENERAL CHARACTERISTICS OF ACTINIDES

Excepting Ac, Th, Pa and U which occur in nature in uranium minerals, all the remaining actinides are unstable and synthetic elements. These have been made by artificial nuclear transmutations. All the actinides are radioactive. Actinides are analogous to lanthanides and involve the filling of 5f-orbitals. The following general characteristics are shown by actinides:

#### 1. Electronic configuration

In lanthanides, after lanthanum 4f-orbitals become appreciably lower in energy than the 5d-orbitals. Thus, in lanthanides the electrons fill the 4f-orbitals in a regular way with minor differences where it is possible to attain a half filled shell. Similarly, it might have been expected that after actinium the 5f-orbitals would become lower in energy than the 6d-orbitals. However, for the first four actinide elements, Th, Pa, U and Np the difference in energy between 5f and 6d-orbitals is small. Thus, in these elements (and their ions) electrons may occupy the 5f or the 6d levels or sometimes both. Later in the actinide series the 5f-orbitals do become appreciably lower in energy. Thus, from Pu onwards the 5f-shell fills in a regular way and the elements become very similar. The most widely accepted electronic configurations of actinides are tabulated below. The general electronic configurations of actinides may be written as:

$$[Rn]5f^{1-14}6d^{0,1}7s^2$$

Name of the element	Symbol	Atomic number	Electronic configuration	Oxidation states
Actinium	Ac	89	$[Rn]6d^{1},7s^{2}$	+3
Thorium	Th	90	$[Rn]6d^2,7s^2$	+3, +4
Protactinium	Pa	91	$[Rn]5f^2,6d^1,7s^2$	+3, +4, +5
Uranium	U	92	$[Rn]5f^3,6d^1,7s^2$	+3, +4, +5, +6
Neptunium	_ Np	93	$[Rn]5f^4,6d^1,7s^2$	+3, +4, +5, +6, +7

Plutonium	Pu	94	$[Rn]5f^6,7s^2$	+3, +4, +5, +6, +7
Americium	Am	95	$[Rn]5f^7,7s^2$	+2, +3, +4, +5, +6
Curium	Cm	96	$[Rn]5f^7,6d^1,7s^2$	+3, +4
Berkelium	Bk	97	$[Rn]5f^9,7s^2$	+3, +4
Californium	Cf	98	$[Rn]5f^{10},7s^2$	+2, +3
Einsteinium	Es	99	$[Rn]5f^{11},7s^2$	+2, +3
Fermium	Fm	100	$[Rn]5f^{12},7s^2$	+2, +3
Mendelevium	Md	101	$[Rn]5f^{13},7s^2$	+2, +3
Nobelium	No	102	$[Rn]5f^{14},7s^2$	+2, +3
Lawrencium	Lr	103	$[Rn]5f^{14},6d^1,7s^2$	+3

#### 2. Oxidation states

The known oxidation states of the actinide elements are shown in the above table. The actinides exhibit most common oxidation state of +3 like the lanthanides. However, this state is not always most stable as for the first four elements (Th, Pa, U and Np). For example, U<sup>3+</sup> is readily oxidised in air and in solution. +3 state is the most stable state for the later elements  $Am \rightarrow Lr$  (except No). The most stable oxidation states for the first four elements are Th (+4), Pa (+5) and U (+6). These high oxidation states involve using all the outer electrons including f electrons for bonding. Though Np shows +7 oxidation state but it is oxidising and the most stable state for Np is +5. Pu shows all the oxidation states from +3 to +7 but the most stable is +4. Am shows oxidation states from +2 to +6. Am<sup>2+</sup> has an  $f^7$  configuration. It is the analogue of Eu<sup>2+</sup> but it only exists in solid as fluoride. However, for Am and almost all the remaining elements +3 state is most stable.

+4 oxidation state exists for all the elements from Th to Bk.  $Cf^{2+}$ ,  $Es^{2+}$ ,  $Fm^{2+}$ ,  $Md^{2+}$  and  $No^{2+}$  exist as ions in solution. Their properties are like alkaline earth metals particularly  $Ba^{2+}$ . It is the most stable state for No and corresponds to an  $f^{14}$  configuration.

+5 oxidation state occurs for the elements  $Pa \to Am$ . A few solid compounds are known in +5 oxidation state but  $M^{5+}$  ions do not occur in solution. However,  $MO_2^+$  ions exist between pH 2-4. These ions disproportionate rapidly in solution.

$$2UO_{2}^{+} + 4H^{+} \longrightarrow U_{(+4)}^{4+} + UO_{2}^{2+} + 2H_{2}O$$

+6 oxidation state occurs as fluorides,  $MF_6$ , for the elements U, Np, Pu and Am. The +6 state is more widely found as the dioxoion,  $MO_2^{2+}$ . The ion is stable and exists both in solution and in crystals.

The 5f-orbitals extend into space beyond the 6s and 6p-orbitals and participate in bonding. This is in direct contrast to the lanthanides where the 4f-orbitals are buried deep inside in the atom, totally shielded by outer orbitals and thus unable to take part in bonding. The participation of the 5f-orbitals explains the higher oxidation states shown by earlier actinide elements.

The lower oxidation states tend to be ionic and the higher ones are covalent.  $M^{2+}$ ,  $M^{3+}$  and  $M^{4+}$  ions are known. Hydrolysis of these ions occurs quite readily but can be suppressed by using acid solutions. Hydrolysis of compounds in the higher oxidation states gives  $+5-MO_2^+$  ions and  $+6-MO_2^{2+}$  ions.

#### 3. Physical properties

The elements are all silvery metals. The melting points are moderately high but are considerably lower than those of transition elements. The size of the ions decreases gradually along the series because the extra charge on the nucleus is poorly screened by the f electrons. This results in an 'actinide contraction' similar to the lanthanide contraction. Actinides have high densities. Some properties of the actinides up to berkelium are tabulated below. Not much information is available about heavy actinides.

Element	Melting point (°C)	Density (g cm <sup>-3</sup> )	Radius M <sup>3+</sup> (pm)	Radius M <sup>4+</sup> (pm)
Thorium	1750	11.8	108	94
Protactinium	n 1552	15.4	104	90
Uranium	1130	19:1	102.5	89
Neptunium	640	20.5	101	87
Plutonium	640	19.9	100	86
Americium	1170	13.7	97.5	85
Curium	1340	13.5	97	85
Berkelium	986	14.8	96	83 .

#### 4. Colour of the ions

Actinide ions are generally coloured. The colour of the ions depends on the number of electrons present in 5f-orbitals. The ions having no electron in 5f-orbitals (*i.e.*, 5f<sup>0</sup>) or seven electrons in 5f-orbitals (*i.e.*, 5f<sup>7</sup>) are colourless. The ions having 2 to 6 electrons in 5f-orbitals are coloured both in the crystalline and in aqueous solution. The colour is due to f-f transition.

$${
m Th}^{4+}$$
  ${
m U}^{3+}$   ${
m Np}^{3+}$   ${
m Pu}^{3+}$   ${
m Am}^{3+}$   ${
m Cm}^{3+}$   ${
m U}^{4+}$   ${
m Np}^{4+}$   $(5f^0)$   $(5f^3)$   $(5f^4)$   $(5f^5)$   $(5f^6)$   $(5f^7)$   $(5f^2)$   $(5f^3)$  Colour- Red Purple Violet Pink Colour- Green Yellow less green

#### 5. Magnetic behaviour

Majority of the ions of the actinides possess unpaired electrons, thus they are paramagnetic in nature. Th<sup>3+</sup>(5 $f^1$ ), Pa<sup>4+</sup>(5 $f^1$ ), U<sup>3+</sup>(5 $f^3$ ), Np<sup>5+</sup>(5 $f^2$ ), Pu<sup>4+</sup>(5 $f^4$ ), Am<sup>5+</sup>(5 $f^4$ ), etc., are paramagnetic. Cations of actinides which contain only paired electrons are diamagnetic. Ac<sup>3+</sup>(5 $f^0$ ), Th<sup>4+</sup>(5 $f^0$ ), U<sup>6+</sup>(5 $f^0$ ), Lr<sup>3+</sup>(5 $f^{14}$ ), etc., are diamagnetic in nature.

#### 6. Formation of complexes

Actinides have somewhat higher tendency to form complex compounds in comparison to lanthanides. This is due to their higher charge and smaller size of their ions. Most of the halides of actinides form complex compounds with alkali metal halides. Actinides form chelates with organic compounds such as EDTA and oxine. The degree of complex formation for the ions  $M^{4+}$ ,  $MO_2^{2+}$ ,  $M^{3+}$  and  $MO_2^{+}$  decreases in the order

$$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$$

#### 7. Chemical Reactivity

On account of low ionisation energies, the actinides are highly electropositive metals. They react with hot water and tarnish in air forming an oxide coating. The metals react readily with HCl but reactions with other acids are slower than expected. Concentrated HNO<sub>3</sub> makes Th, U and Pu passive. The metals react with oxygen, the halogens and hydrogen. Actinides act as strong reducing agents.

#### 8. Radioactivity

All the actinide elements are radioactive in nature.

#### **■** Uses of Actinides

Thorium, uranium and plutonium are three actinides which find uses as such or in the form of compounds.

- (i) Uses of thorium: (a) When thorium dioxide containing 1% CeO<sub>2</sub> is heated in a gas flame, it emits a brilliant white light. Because of this, it is used for making incandescent gas mantles. The mantle made from silk fibre is treated with a mixed solution of 99% thorium nitrate and 1% cerium nitrate. When this mantle is fixed in the lamp and ignited, the silk fibre burns away leaving behind a network of thoria (ThO<sub>2</sub>) and ceria (CeO<sub>2</sub>).
- (b) Naturally occurring thorium is almost entirely Th-232. This isotope is not fissionable but is converted into U-233 which is fissionable.

$$^{232}_{90}$$
Th +  $^{1}_{0}n$   $\longrightarrow$   $^{233}_{90}$ Th  $\stackrel{-\beta}{\longrightarrow}$   $^{233}_{91}$ Pa  $\stackrel{-\beta}{\longrightarrow}$   $^{233}_{92}$ U

Thus, thorium is used for the production of fissionable material needed for atomic reactors,

- (c) Thorium salts are used in medicines for the treatment of cancer.
- (ii) Uses of uranium: (a) The salts of uranium find use in glass industry (for imparting green colour), textile industry, ceramic industry and in medicines.
- (b) The U-235 isotope is used as nuclear fuel in atomic reactors and atom bombs.
- (iii) Uses of plutonium: Pu-239 is used as a nuclear fuel. It is obtained from U-238.

### 14.29

# COMPARISON OF LANTHANIDES AND ACTINIDES

Both lanthanides and actinides are f-block elements, *i.e.*, they involve filling of the f-subshell in the ante-penultimate shells of their atoms. Their general electronic configuration can be written as:

$$(n-2)f^{1-14}(n-1)d^{0,1}ns^2$$

where n = 6 for lanthanides and n = 7 for actinides. Due to similar electronic configuration, they show similarities in properties but differ also in some of their characteristics.

#### Similarities

- (i) In the atoms of the elements of both the series, three outermost shells are partly filled while the remaining innershells are completely filled. Two electrons are present in the outermost energy shell, 18 or 19 electrons are present in the penultimate energy shell  $[(n-1)s^2p^6d^{0,1}]$  and next to the penultimate shell contains 18 to 32 electrons  $[(n-2)s^2p^6d^{10}f^{1-14}]$ . However, in two elements lutetium and lawrencium the f-subshell is completely filled. These are the end members of the two series.
- (ii) The elements of both the series show mainly +3 oxidation state.
- (iii) The elements of both the series are electropositive in nature. They are reactive metals and act as strong reducing agents.
- (iv) In both the series, there is contraction in atomic and ionic  $(M^{3+}$  ions) size as the atomic number increases, *i.e.*, like lanthanide contraction, there is actinide contraction. These contractions are due to the poor shielding effect between the electrons residing in (n-2)f-orbitals.
- (v) Cations with unpaired electrons in both the series are paramagnetic.
- (vi) Most of the cations of lanthanides and actinides are coloured. The cations having same number of unpaired electrons have almost same absorption spectra. Sharp line like bands are observed in both the series. These are due to the jump of an electron from one energy level to another within (n-2)f-orbitals.
- (vii) The nitrates, perchlorates and sulphates of trivalent actinides as well as lanthanides are soluble while the hydroxides, carbonates, fluorides of the elements of both the series are insoluble.
- (viii) Ion exchange behaviour is exhibited by both actinides and lanthanides.

#### Dissimilarities

Differences in some of the characteristics of lanthanides and actinides are given in the table which is on next page.

S. No.	Lanthanides	Actinides
(i)	Except promethium, all the remaining lanthanides are non-radioactive.	All the actinides are radioactive.
(ii)	Besides +3 oxidation state, lan- thanides in some cases show +2 and +4 oxidation states.	Besides +3 oxidation state, actinides show a variety of oxidation states like +2, +4, +5, +6 and +7 also.
(iii)	anthanides do not form oxo-	Actinides form oxo-ions such as $UO_2^{2+}$ , $PuO_2^{2+}$ , $UO_2^{+}$ , $UO_2^{+}$ , etc. These ions are stable in acid and aqueous solutions.

(iv)	Oxides and hydroxides of lanthanides are less basic.	Oxides and hydroxides of actinides are more basic.
(v)		Actinides have more tendency to form complex compounds on account of high charge density.
(vi)	The magnetic nature (parama-	The magnetic nature (paramagnetic) cannot be explained easily. The observed values usually do not tally with expected values.
(vii)	Most of the tripositive ions are colourless.	Most of the tripositive and tetrapositive ions are coloured.

# 

**Example 1.** Give the number of unpaired electrons in the following:

(i) 
$$Cr^{2+}$$
 (Z = 24) (ii)  $Fe^{2+}$  (Z =

(iii) 
$$Mn^{2+}$$
 (Z = 25) (iv)  $Ti^{4+}$  (Z = 22)

llowing:  
(i) 
$$Cr^{2+}$$
 (Z = 24) (ii)  $Fe^{2+}$  (Z = 26)  
(iii)  $Mn^{2+}$  (Z = 25) (iv)  $Ti^{4+}$  (Z = 22)  
(v)  $La^{3+}$  (Z = 57) (vi)  $Zn^{2+}$  (Z = 30)  
**Solution:**

3 <i>d</i>
Electronic configuration of $Cr^{2+} = 3d^4$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$
Unpaired electrons = $4$ 3d
Electronic configuration of $Fe^{2+} = 3d^6$ $\uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow$
Unpaired electrons = $4$ 3d
Electronic configuration of $Mn^{2+} = 3d^5$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$
Unpaired electrons = 5
Electronic configuration of $\text{Ti}^{4+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^0, 4s^0$
Unpaired electrons = 0
Electronic configuration of $La^{3+} = 2, 8, 18, 18, 8+5d^0, 6s^0$
Unpaired electrons = 0
Electronic configuration of $Zn^{2+} = 2$ , 8, 8 + $3d^{10}$ 3d
Unpaired electrons = 0

**Example 2.** Why does Mn (II) show maximum paramagnetic character amongst the bivalent ions of the first transition series? Calculate the theoretical value of magnetic moment.

#### **Solution:**

The value of paramagnetic nature depends on the number of unpaired orbitals. Mn (II) possesses maximum number of unpaired orbitals amongst divalent ions of the first transition series and thus, possess maximum value of paramagnetic character.

Theoretical value of magnetic moment = 
$$\sqrt{n(n+2)}$$
  
=  $\sqrt{5 \times 7}$  as  $n = 5$   
=  $\sqrt{35}$  = 5.91 B.M.

#### **Example 3.** Answer the following:

- (i) Which one of  $Fe^{2+}$  and  $Fe^{3+}$  ions is more paramagnetic and why?
- (ii) Which of the following ions are expected to be coloured and why?

 $Cu^{+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Cr^{3+}$ ,  $Sc^{3+}$ ,  $Ti^{4+}$ 

- (iii) Name the two elements of first transition series which have abnormal electronic configuration and why?
- (iv) Name the lightest and heaviest elements in terms of density among the transition elements.
- (v) How many elements are present in each transition series? Why this number cannot be less or more?

#### **Solution:**

- (i) Fe<sup>3+</sup> is more paramagnetic than Fe<sup>2+</sup> as Fe<sup>3+</sup> consists five unpaired electrons while Fe<sup>2+</sup> possesses four unpaired electrons.
- (ii) Any ion of transition elements which possesses unpaired d electrons, i.e., d-d transition is possible shows a characteristic colour.  $(n-1)d^0$  or  $(n-1)d^{10}$  configuration does not involve d-d transition and hence, is colourless.

Fe<sup>2+</sup>, Mn<sup>2+</sup> and Cr<sup>3+</sup> are coloured, while Cu<sup>+</sup>, Sc<sup>3+</sup> and Ti<sup>4+</sup> are colourless.

Ion	Configuration	Ion	Configuration,
Cu <sup>+</sup>	$3d^{10}$ (colourless);	Cr <sup>3+</sup>	$3d^3$ (coloured)
Fe <sup>2+</sup>	$3d^6$ (coloured);	Sc <sup>3+</sup>	3d <sup>0</sup> (colourless)
Mn <sup>2+</sup>	$3d^5$ (coloured);	Ti <sup>4+</sup>	$3d^0$ (colourless)

(iii) Chromium and copper.

Chromium attains  $3d^5,4s^1$  configuration in which all the dorbitals are unpaired in order to get extra stability.

Copper attains  $3d^{10}.4s^1$  configuration in which all the dorbitals are paired in order to get extra stability.

(iv) Lightest element—Scandium; Heaviest element—Osmium

(v) Each transition series consists ten elements. This number cannot be 9 or 11 as the maximum capacity of *d*-orbitals is of 10 electrons which are gradually filled up.

1st Tr. series  $3d^{1-10}$  Ten elements 2nd Tr. series  $4d^{1-10}$  Ten elements 3rd Tr. series  $5d^{1-10}$  Ten elements

#### **Example 4.** What happens when?

- (i) Ferric chloride is added to potassium ferrocyanide.
- (ii) Iron reacts with cold dilute nitric acid. [LI.T. 1990]
- (iii) Potassium ferricyanide is added to ferrous sulphate.
- (iv) Excess of potassium iodide is added to mercuric chloride.
- (v) Green vitriol is strongly heated. [Roorkee 1990]
- (vi) Silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium. [M.L.N.R. 1996]
- (vii)Zinc oxide is treated with excess of sodium hydroxide solution.
- (viii) Ammonium thiocyanate is added to ferric chloride solution.

#### Solution:

(i) Prussian blue is formed.

$$4\text{FeCl}_3 + 3\text{K}_4\text{Fe}(\text{CN})_6 \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl}$$
Prussian blue
(Ferri ferrocyanide)

(ii) Ammonium nitrate is formed.

[Fe + 2HNO<sub>3</sub> 
$$\longrightarrow$$
 Fe(NO<sub>3</sub>)<sub>2</sub> + 2H] × 4  
HNO<sub>3</sub> + 8H  $\longrightarrow$  NH<sub>3</sub> + 3H<sub>2</sub>O  
NH<sub>3</sub> + HNO<sub>3</sub>  $\longrightarrow$  NH<sub>4</sub>NO<sub>3</sub>

$$4Fe + 10HNO_3 \longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O_3$$

(iii) Ferrous ion is first oxidised to ferric ion while ferricyanide ion is reduced to ferrocyanide ion. Then, ferric ions react with ferrocyanide ions to form potassium ferric ferrocyanide (Turnbull's blue).

$$Fe^{2+} + [Fe(CN)_{6}]^{3-} \longrightarrow Fe^{3+} + [Fe(CN)_{6}]^{4-}$$

$$K^{+} + Fe^{3+} + [Fe(CN)_{6}]^{4-} \longrightarrow K^{+}Fe^{3+}[Fe(CN)_{6}]^{4-}$$
Potassium ferricferrocyanide
(Turnbull's blue)

(iv) First scarlet precipitate is formed which then dissolves in excess of potassium iodide forming a complex.

$$HgCl_2 + 2KI \longrightarrow HgI_2 + 2KCl$$
 $HgI_2 + 2KI \longrightarrow K_2HgI_4$ 
Potassium tetraiodo mercurate
(colourless)

(v) When heated strongly, a mixture of gases consisting SO<sub>2</sub> and SO<sub>3</sub> is evolved and a red residue, Fe<sub>2</sub>O<sub>3</sub> is formed.

$$[FeSO_4 \cdot 7H_2O \longrightarrow FeSO_4 + 7H_2O] \times 2$$

$$2FeSO_4 \longrightarrow Fe_2O_3 + SO_2 + SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$\begin{array}{c}
2\text{FeSO}_4.7\text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{H}_2\text{SO}_4 + 13\text{H}_2\text{O} \\
\text{Green vitriol} & \text{Red}
\end{array}$$

(vi) AgCl dissolves in KCN forming a complex, potassium argentocyanide. The addition of zinc precipitates silver.

$$\begin{array}{ccc} AgCl + 2KCN & \longrightarrow & KAg(CN)_2 + KCl \\ 2KAg(CN)_2 + Zn & \longrightarrow & K_2Zn(CN)_4 + 2Ag \\ & & Potassium \\ & zincocyanide \end{array}$$

(vii) ZnO dissolves in NaOH forming sodium zincate.

$$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$$

(viii) Deep red colouration due to the formation of a complex is developed.

FeCl<sub>3</sub> + NH<sub>4</sub>CNS 
$$\longrightarrow$$
 Fe(CNS)Cl<sub>2</sub> + NH<sub>4</sub>Cl  
or FeCl<sub>3</sub> + 3NH<sub>4</sub>CNS  $\longrightarrow$  Fe(CNS)<sub>3</sub> + 3NH<sub>4</sub>Cl

#### **Example 5.** Explain the following:

- (i) Acidified  $K_2Cr_2O_7$  solution turns green when sodium sulphite is added to it.
- (ii) Partial roasting of sulphide ore is done in the metallurgy of copper.
  - (iii) Zinc becomes dull in moist air.
  - (iv) In the metallurgy of iron, limestone is added to the ore.
- (v) A little acid is always added in the preparation of aqueous ferrous sulphate solution.
- (vi) The addition of NaOH solution to a solution of zinc chloride produces a white precipitate which dissolves on further addition of NaOH.
- (vii) The addition of  $NH_4OH$  to  $ZnSO_4$  solution produces white precipitate but no precipitate is formed if it contains  $NH_4Cl$ .
- (viii) Mercuric chloride and stannous chloride cannot exist as such if present together in an aqueous solution.
- (ix) Zinc and not copper is used for the recovery of silver from complex  $[Ag(CN)_2]^-$ .
- (x) Why is chalcocite roasted and not calcined in the extraction of copper?
- (xi) Copper implements were known to mankind much earlier than iron implements.
- (xii) Copper sulphate dissolves in  $NH_4OH$  solution but  $FeSO_4$  does not.
  - (xiii) A ferrous salt turns brown in air.
  - (xiv) A ferrous salt decolourises acidified KMnO<sub>4</sub> solution.
  - (xv) Cadmium is used to extinguish nuclear fire.
- (xvi) Copper hydroxide is soluble in ammonium hydroxide but not in sodium hydroxide.

#### Solution:

(i) Na<sub>2</sub>SO<sub>3</sub> is a reducing agent. It reduces acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to chromic sulphate which is green in colour.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$
  
 $[Na_2SO_3 + [O] \longrightarrow Na_2SO_4] \times 3$ 

(ii) The concentrated ore is roasted in reverberatory furnace in a current of air. The volatile impurities such as free sulphur, arsenic and antimony are removed as volatile oxides and the ore is partially oxidised.

$$4As + 3O_2 \longrightarrow 2As_2O_3$$

$$4Sb + 3O_2 \longrightarrow 2Sb_2O_3$$

$$S + O_2 \longrightarrow SO_2$$

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

$$2CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

A mixture of sulphides and oxides is formed. The Cu<sub>2</sub>O so formed reacts with unconverted Cu<sub>2</sub>S to form copper.

$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$

(iii) When zinc is exposed to moist air, the surface is affected with the formation of a film of basic zinc carbonate on it. Due to this zinc becomes dull.

$$\begin{array}{c} [2Zn + 2H_2O + O_2 \longrightarrow 2Zn(OH)_2] \times 2 \\ Zn(OH)_2 + CO_2 \longrightarrow ZnCO_3 + H_2O \\ ZnCO_3 + 3Zn(OH)_2 \longrightarrow ZnCO_3 \cdot 3Zn(OH)_2 \\ \hline 4Zn + 3H_2O + CO_2 + 2O_2 \longrightarrow ZnCO_3 \cdot 3Zn(OH)_2 \\ Basic zinc carbonate \\ \end{array}$$

(iv) Limestone is added as a flux. It is decomposed in the furnace into CaO and CO<sub>2</sub>. CaO reacts with gangue silica and forms infusible slag, CaSiO<sub>3</sub>.

$$\begin{array}{c} \text{CaCO}_{3} \longrightarrow \text{CaO} + \text{CO}_{2} \\ \text{CaO} + \text{SiO}_{2} \longrightarrow \text{CaSiO}_{3} \\ \text{Slag} \end{array}$$

(v) Ferrous sulphate is a salt of a weak base and a strong acid. Thus, its hydrolysis occurs when it is dissolved in water and solution becomes turbid due to formation of ferrous hydroxide.

$$FeSO_4 + 2H_2O \implies Fe(OH)_2 + H_2SO_4$$

Addition of a small amount of acid shifts the equilibrium towards left and thus prevents hydrolysis.

(vi) On addition of NaOH, a white precipitate of Zn(OH)<sub>2</sub> is formed which dissolves in excess of NaOH forming sodium zincate.

$$\begin{split} ZnCl_2 + 2NaOH &\longrightarrow Zn(OH)_2 + 2NaCl \\ Zn(OH)_2 + 2NaOH &\longrightarrow Na_2ZnO_2 + 2H_2O \\ &\quad Soluble \end{split}$$

(vii) NH<sub>4</sub>OH is a weak hydroxide. It ionises slightly furnishing OH<sup>-</sup> ions. However, the OH<sup>-</sup> ions are sufficient to cause the precipitation of Zn(OH)<sub>2</sub> as its solubility product is exceeded.

$$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)_2SO_4$$
 White ppt.

In presence of NH<sub>4</sub>Cl, the ionisation of NH<sub>4</sub>OH is further suppressed and sufficient OH<sup>-</sup> ions are not available to cause precipitation as the solubility product is not exceeded.

(viii) HgCl<sub>2</sub> is an oxidising agent while SnCl<sub>2</sub> is a reducing agent. When both are present, a redox reaction occurs forming Hg and stannic chloride as final products.

$$\begin{array}{c} SnCl_2 + 2HgCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4 \\ White \\ Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4 \\ Black \ or \ grey \end{array}$$

(ix) Zinc is cheaper as well as stronger reducing agent in comparison to copper.

$$Zn + 2[Ag(CN)_2]^- \longrightarrow 2Ag + [Zn(CN)_4]^{2-}$$

(x) Air is necessary to convert impurities such as sulphur, arsenic and antimony into volatile oxides and for partial oxidation of the pyrite ore. Calcination does not use oxygen while roasting is done in presence of air. Thus, roasting and not calcination is done in the metallurgy of copper.

See reactions in answer (ii).

- (xi) Copper occurs in nature also as a free metal but iron is always found in nature in combined state. The technology to manufacture iron was developed much later. Hence iron implements were used later than copper implements as copper was known in the early times.
- (xii) Copper sulphate dissolves in the ammonium hydroxide due to formation of a copper complex. Ferrous sulphate reacts with NH<sub>4</sub>OH to form insoluble Fe(OH)<sub>2</sub>. It does not form any complex with NH<sub>4</sub>OH.

$$\begin{array}{c} CuSO_4 + 4NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O \\ & \text{Deep blue solution} \end{array}$$
 
$$FeSO_4 + 2NH_4OH \longrightarrow Fe(OH)_2 + (NH_4)_2SO_4$$
 Insoluble

(xiii) A ferrous salt turns brown in air due to oxidation to ferric salt.

(xiv) Ferrous salt acts as a reducing agent. It reduces acidified KMnO<sub>4</sub> into K<sub>2</sub>SO<sub>4</sub> and MnSO<sub>4</sub> which form colourless solution, *i.e.*, decolourisation of KMnO<sub>4</sub> solution takes place.

$$\begin{array}{c} 2KMnO_4 + 3H_2SO_4. \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \\ \underline{ [2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5} \\ \hline 2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 \\ + 5Fe_2(SO_4)_3 + 8H_2O \\ \end{array}$$

(xv) Cadmium absorbs neutrons, stops nuclear fission reaction and extinguishes nuclear fire.

(xvi)  $Cu(OH)_2$  dissolves in  $NH_4OH$  by forming a complex.  $Cu(OH)_2 + 4NH_4OH \longrightarrow [Cu(NH_3)_4](OH)_2 + 4H_2O$  $Cu(OH)_2$  is insoluble in NaOH as no such complex is formed.

#### **Example 6.** Explain the following:

- (i) Magnesium oxide is used for lining of steel making furnace.
  - (ii) Cast iron is hard but pure iron is soft in nature.
  - (iii)  $Fe^{3+}$  is more stable than  $Fe^{2+}$ .

- (iv) Anhydrous FeCl<sub>3</sub> cannot be obtained by heating hydrated ferric chloride.
  - (v) The compounds of iron are coloured and paramagnetic.
  - (vi) Mercuric chloride is called corrosive sublimate.
- (vii) The colour of mercurous chloride changes from white to black when treated with ammonia solution.
  - (viii) Excess of carbon is added in the zinc metallurgy.
- (ix) Zinc readily liberates hydrogen from cold dilute  $H_2SO_4$  but not from cold concentrated  $H_2SO_4$ .
  - (x) The compounds of Zn, Cd and Hg are usually white.
- (xi) A dark blue precipitate is formed when sodium hydroxide solution is added to copper sulphate solution. The precipitate darkens on heating.
- (xii) Cuprous chloride is insoluble in water and dilute HCl but dissolves in concentrated HCl.
- (xiii) CuS is not precipitated by passing  $H_2S$  through copper sulphate solution containing KCN.
  - (xiv) Silver nitrate solution is kept in dark coloured bottles. **Solution:**
- (i) MgO is basic in nature. It removes acidic impurities present in cast iron used for making steels.

$$MgO + SiO_2 \longrightarrow MgSiO_3$$
  
 $Slag$   
 $3MgO + P_2O_5 \longrightarrow Mg_3(PO_4)_2$ 

MgO is also a refractory material as it can tolerate very high temperature of the furnace.

- (ii) Cast iron consists carbon 2.5 to 5% which is responsible for its hardness.
- (iii) Fe<sup>3+</sup> has the configuration [Ar] $3d^5$ , *i.e.*, all the five d-orbitals are singly occupied which is a stable configuration in accordance to Hund's rule of maximum multiplicity while the configuration of Fe<sup>2+</sup> is [Ar]  $3d^6$  in which one orbital is doubly occupied and rest of the four orbitals are singly occupied. It is not so stable configuration as it is unsymmetrical in nature.
- (iv) On heating hydrated ferric chloride, anhydrous ferric chloride is not formed as water of crystallisation reacts to form  $Fe_2O_3$  and HCl.
- (v) Iron compounds either has  $Fe^{2+}$  or  $Fe^{3+}$  ions and each contains unpaired orbitals which show paramagnetic character. d-d transition is possible. Hence, the compounds are coloured.
- (vi) HgCl<sub>2</sub> is poisonous (corrosive) in nature. It undergoes sublimation. Due to these properties, it is called corrosive sublimate.
- (vii) Hg<sub>2</sub>Cl<sub>2</sub> reacts with NH<sub>3</sub> to form a mixture of mercury and mercuric amino chloride which is a black substance.

$$\begin{array}{ccc} Hg_2Cl_2 + NH_3 & \longrightarrow & \underbrace{Hg + Hg(NH_2)Cl}_{Black} + HCl \end{array}$$

- (viii) Carbon has to play a double role,
  - (a) It reduces zinc oxide to zinc.

. 
$$ZnO + C \longrightarrow Zn + CO$$
  
 $ZnO + CO \longrightarrow Zn + CO_2$ 

- (b) It reduces  $CO_2$  into CO which is used as a fuel  $CO_2 + C \longrightarrow 2CO$
- (ix)  $H_2SO_4$  is a covalent compound. Conc.  $H_2SO_4$  does not contain  $H_3O^+$  ions while dilute  $H_2SO_4$  consists  $H_3O^+$  ions which react with zinc to liberate hydrogen.

$$H_2SO_4 + 2H_2O \implies 2H_3O^+ + SO_4^{2-}$$
  
 $Zn + 2H_3O^+ \longrightarrow Zn^{2+} + H_2 + 2H_2O$ 

- (x) In the compounds of zinc metals,  $M^{2+}$  ions possess the penultimate *d*-orbitals doubly occupied, *i.e.*,  $(n-1)d^{10}$  configuration. There is no d-d transition. Hence, the compounds of zinc metals are colourless.
- (xi) NaOH reacts with CuSO<sub>4</sub> when dark blue precipitate of Cu(OH)<sub>2</sub> is formed. This precipitate on heating forms CuO which is black in colour. Hence, the colour darkens on heating.

$$\begin{array}{c} \text{CuSO}_4 + 2\text{NaOH} & \longrightarrow \text{Cu(OH)}_2 + \underbrace{\text{Na}_2\text{SO}_4}_{\text{Blue}} \\ \text{Cu(OH)}_2 & \longrightarrow \text{CuO}_{\text{Black}} + \text{H}_2\text{O} \end{array}$$

(xii) Cu<sub>2</sub>Cl<sub>2</sub> dissolves in conc. HCl due to the formation of a copper complex.

$$Cu_2Cl_2 + 2HCl \longrightarrow 2H[CuCl_2]$$

(xiii) CuSO<sub>4</sub> forms a complex with KCN.

$$CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4$$

$$2Cu(CN)_2 \longrightarrow Cu_2(CN)_2 + (CN)_2$$

 $Cu_2(CN)_2+6KCN \longrightarrow 2K_3Cu(CN)_4 \Longrightarrow 6K^++2[Cu(CN)_4]^{3-}$  $K_3Cu(CN)_4$  complex does not furnish  $Cu^{2+}$  ions. Hence, no precipitate of CuS is formed when  $H_2S$  is passed through

solution.

(xiv) AgNO<sub>3</sub> is photosensitive. It decomposes in presence of light. To prevent its decomposition, it is kept in coloured bottles as these do not permit light to pass through.

#### **Example 7.** Explain the following:

- (i) Copper (I) salts are not known in aqueous solutions.
- (ii) Ferric iodide is very unstable but ferric chloride is not.
- (iii) Silver bromide is used in photography.
- (iv) Anode mud in copper refining contains silver and gold.
- (v) Silver fluoride is fairly soluble in water while other silver halides are insoluble.
- (vi) Copper is regarded as transition metal though it has completely filled d-orbital (d<sup>10</sup>). [M.L.N.R. 1994]
- (vii) Out of cobalt and zinc salts, which is attracted in a magnetic field? [Roorkee 1995]
  - (viii) The species  $[CuCl_4]^{2-}$  exist but  $[Cul_4]^{2-}$  does not.
  - (ix) Copper is largely used in electrical wiring.
  - (x) A solution of  $K_2CrO_4$  changes colour on being acidified. **Solution:**
- (i) Cu (I) salts undergo disproportionation in aqueous solution.

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

(ii) I<sup>-</sup> ion is a stronger reducing agent in comparison to Cl<sup>-</sup> ion. Fe<sup>3+</sup> is easily reduced by iodide ion.

$$2Fe^{3+} + 2I^{-} \longrightarrow 2Fe^{2+} + I_{2}$$

- (iii) AgBr is sensitive to light. It is converted into metallic silver grains when light is incident on it.
- (iv) Silver and gold are less basic than copper. These are not ionised under the applied voltage and get deposited in the anodic mud.
- (v) The hydration energy of AgF is higher than its lattice energy. Hence, it is soluble in water. The hydration energy values of other halides are smaller than their lattice energy values. Hence, these halides are insoluble in water.
- (vi) Although copper has  $3d^{10}$  configuration yet it can lose one electron from this arrangement. Thus,  $Cu^{2+}$  ion has  $3d^9$  configuration. So, according to the definition that transition metal cations have partially filled (n-1)d-subshell, copper is regarded as a transition metal.
- (vii) Of cobalt and zinc salts, the cobalt salts are attracted in a magnetic field, because cobalt ion containing unpaired electrons is characterised by a permanent magnetic moment.  $Zn^{2+}$  ion contains  $3d^{10}$  configuration, *i.e.*, no unpaired electrons, so zinc salts are not attracted in magnetic field.
- (viii) I<sup>-</sup> ion is a stronger reducing agent than CI<sup>-</sup> ion. It reduces Cu<sup>2+</sup> ion into Cu<sup>+</sup> ion. Hence, cupric iodide is converted into cuprous iodide. Thus, the species [CuI<sub>4</sub>]<sup>2-</sup> does not exist.
- (ix) Copper is a very good conductor of electricity. Moreover, it is not easily affected by the atmosphere.
- (x) On being acidified, the chromate ions dimerise to form dichromate ions which are orange coloured. Thus,

**Example 8.** How the following conversions are made? Explain only by giving chemical equations.

- (i) Copper chloride from copper nitrate.
- (ii) Cuprous oxide from copper sulphate.
- (iii) Cuprous oxide from copper.
- (iv) Mercuric chloride from mercuric sulphate.
- (v) Anhydrous ZnCl<sub>2</sub> from white vitriol.
- (vi) Zinc carbonate from zinc oxide.
- (vii) Ferrous sulphate from ferrous ammonium sulphate.
- (viii) Prussian blue from K<sub>4</sub>Fe(CN)<sub>6</sub>.
- (ix) Lithopone from white vitriol.
- (x) Cuprous iodide from copper sulphate.

#### Solution:

(i) 
$$Cu(NO_3)_2 + 2NaOH \longrightarrow Cu(OH)_2 + 2NaNO_3$$

(ii) 
$$Cu(OH)_2 + 2HCI \longrightarrow CuCl_2 + 2H_2O$$
  
 $CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$ 

$$Cu(OH)_2 \xrightarrow{Strongly} CuO + H_2O$$

$$\begin{array}{cccc} \text{CuO} + \underset{\text{Powder}}{\text{Cu}} & \xrightarrow{\text{Heat}} & \text{Cu}_2\text{O} \\ \\ \text{or} & \text{CuSO}_4 & \longrightarrow & \text{Fehling's solution} \\ \text{C}_6\text{H}_{12}\text{O}_6 + & \text{Fehling's soln.} & \longrightarrow & \text{Cu}_2\text{O} + \text{C}_6\text{H}_{12}\text{O}_7 \\ \\ \text{Glucose} & \text{Red ppt. Gluconic acid} \\ \\ \text{(iii)}\text{Cu} + & \text{4HNO}_3 \text{ (conc.)} & \longrightarrow & \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O} \\ \\ & & 2\text{Cu}(\text{NO}_3)_2 & \xrightarrow{\text{Heat}} & 2\text{CuO} + 4\text{NO}_2 + \text{O}_2^\circ \\ \\ & & \text{CuO} + \text{Cu} & \xrightarrow{\text{Heat}} & \text{Cu}_2\text{O} \end{array}$$

(iv) By heating a solid mixture of HgSO<sub>4</sub> and NaCl.

$$HgSO_4 + 2NaCl \xrightarrow{Heat} HgCl_2 + Na_2SO_4$$

(v) 
$$ZnSO_4.7H_2O \xrightarrow{Strongly} ZnSO_4 + 7H_2O$$
White vitriol  $\xrightarrow{heated} Anhydrous$ 

$$ZnSO_4 \xrightarrow{Heat} ZnO + SO_3 ...$$
  
 $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$ 

$$ZnCl_2 + 2NH_4Cl \xrightarrow{\hspace*{1cm}} ZnCl_2 \cdot 2NH_4Cl \xrightarrow{\hspace*{1cm} Double \hspace*{1cm} salt}$$

$$ZnCl_2 \cdot 2NH_4Cl \xrightarrow{\text{Heat} \atop \text{HCl gas}} ZnCl_2 + 2NH_4Cl$$
Anhydrous

(vi) 
$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$
  
 $ZnSO_4 + 2NaHCO_3 \longrightarrow ZnCO_3 + Na2SO4 + H2O + CO2$ 

(vii) 
$$FeSO_4$$
·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O + 4NaOH  $\longrightarrow$   
 $Fe(OH)_2 + 2NH_3 + 2Na_2SO_4 + 8H_2O$ 
ppt.

$$Fe(OH)_2 + H_2SO_4 \longrightarrow FeSO_4 + 2H_2O$$

The solution is put to crystallisation when crystals of ferrous sulphate, FeSO<sub>4</sub>·7H<sub>2</sub>O, are obtained.

(viii) 
$$4\text{FeCl}_3 + 3\text{K}_4\text{Fe}(\text{CN})_6 \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl}$$
  
Prussian blue

(ix) 
$$ZnSO_4 + BaS \longrightarrow ZnS + BaSO_4$$
  
Lithopone

$$(x) \qquad \qquad 2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$
 White ppt.

**Example 9.** A metal chloride (x) shows the following reactions:

- (a) When  $H_2S$  is passed in an acidified solution of (x) a black precipitate is obtained.
- (b) The black precipitate is not soluble in ammonium sulphide.
- (c) The solution of stannous chloride is added to an aqueous solution of (x), a white precipitate is obtained which turns grey on addition of more stannous chloride.
- (d) When aqueous solution of KI is added to an aqueous solution of (x), a red precipitate is obtained which dissolves on addition of excess of KI.

Identify (x) and write down the equations for the reactions.

[Roorkee 1991]

#### **Solution:**

The acidified solution of (x) gives a black sulphide with  $H_2S$  indicates that the chloride is of a basic cation of second group.

The sulphide is insoluble in ammonium sulphide, hence, the cation belongs to IIA group of mixture analysis.

It gives white precipitate with  $SnCl_2$  which turns to grey in excess of  $SnCl_2$  suggests that (x) is  $HgCl_2$ . It is further confirmed by the reaction with KI.

$$\begin{array}{c} \textbf{Reactions} \ : \ HgCl_2 + H_2S \longrightarrow \underset{Black}{HgS} + 2HCl \\ & Black \\ \\ 2HgCl_2 + SnCl_2 \longrightarrow \underset{White}{Hg_2Cl_2} + SnCl_4 \\ & White \\ \\ Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4 \\ & Grey \\ \\ HgCl_2 + 2KI \longrightarrow \underset{Red \ ppt.}{HgI_2} + 2KCl \\ & Red \ ppt. \\ \\ HgI_2 + 2KI \longrightarrow \underset{Soluble}{K_2HgI_4} \\ & Soluble \\ \end{array}$$

**Example 10.** A certain inorganic compound (A) on heating loses its water of crystallisation. On further heating, a blackish brown powder (B) and two oxides of sulphur (C and D) are obtained. The powder (B) on boiling with hydrochloric acid gives a yellow solution (E). When H<sub>2</sub>S is passed in (E), a white turbidity (F) and apple green solution (G) are obtained. The solution (E) on treatment with thiocyanate ions gives a blood red coloured compound (H). Identify the compounds from (A) to (H).

#### **Solution:**

The compound (A) on strong heating gives two oxides of sulphur, it may be a sulphate. The solution (E) on treatment with thiocyanate ions gives blood red coloured compound (H) indicates that the solution (E) consists  $Fe^{3+}$  ions. Thus, the compound (A) is ferrous sulphate,  $FeSO_4.7H_2O$ .

#### Reactions:

$$\begin{array}{c} \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{-7\text{H}_2\text{O}} \text{FeSO}_4 \xrightarrow{\text{Heat}} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3 \\ (B) & (C) & (D) \\ & & \text{Blackish} \\ & \text{brown powder} \end{array}$$
 
$$\begin{array}{c} \text{Fe}_2\text{O}_3 + 6\text{HCl} \longrightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} \\ (B) & (E) \\ & \text{Yellow solution} \end{array}$$
 
$$2\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow 2\text{FeCl}_2 + 2\text{HCl} + \text{S} \\ (G) & (F) \\ & \text{Apple} & \text{White} \\ & \text{green solution} & \text{turbidity} \end{array}$$
 
$$\begin{array}{c} \text{FeCl}_3 + 3\text{CNS}^- \longrightarrow \text{Fe}(\text{CNS})_3 + 3\text{Cl}^- \\ & \text{Blood red} \\ & \text{coloured solution} \end{array}$$

**Example 11.** (i) A black mineral (A) on treatment with dilute sodium cyanide solution in presence of air gives a clear solution of (B) and (C).

- (ii) The solution (B) on reaction with zinc gives precipitate of a metal (D).
- (iii) (D) is dissolved in dilute  $HNO_3$  and the resulting solution gives a white precipitate (E) with dilute HCl.
  - (iv) (E) on fusion with sodium carbonate gives (D).

(v) (E) dissolves in ammonia solution giving a colourless solution of (F). Identify (A) to (F) and give chemical equations for reactions at steps (i) to (v). [Roorkee 1995]

#### **Solution:**

On the basis of the given data, the black mineral (A) is silver glance, Ag<sub>2</sub>S. It is confirmed by the following:

(i) It dissolves in sodium cyanide solution in presence of air.

$$\begin{array}{c} \operatorname{Ag_2S} + 4\operatorname{NaCN} + 2\operatorname{O}_2 \longrightarrow 2[\operatorname{NaAg}(\operatorname{CN})_2] + \operatorname{Na_2SO_4} \\ \operatorname{Sodium} \\ \operatorname{argento\ cyanide} \\ \operatorname{(B)} \\ \operatorname{(C)} \\ \operatorname{Sodium} \\ \operatorname{sulphate} \\ \operatorname{(C)} \\ \operatorname{Sodium} \\ \operatorname{sulphate} \\ \operatorname{(C)} \\ \operatorname{(E)} \\ \operatorname{(D)} \\ \operatorname{AgR}(\operatorname{CN})_2] + \operatorname{Zn} \longrightarrow \operatorname{Na_2Zn}(\operatorname{CN})_4 + 2\operatorname{Ag} \\ \operatorname{(D)} \\ \operatorname{AgR}(\operatorname{CN})_2] + \operatorname{Zn} \longrightarrow \operatorname{Na_2Zn}(\operatorname{CN})_4 + 2\operatorname{Ag} \\ \operatorname{(D)} \\ \operatorname{AgR}(\operatorname{CN})_2] + \operatorname{Zn} \longrightarrow \operatorname{AgR}(\operatorname{CN})_4 + 2\operatorname{Ag} \\ \operatorname{(D)} \\ \operatorname{AgR}(\operatorname{CN})_2 + \operatorname{AgR}(\operatorname{CN})_3 + \operatorname{NO} + 2\operatorname{H_2O} \\ \operatorname{(D)} \\ \operatorname{AgCl} + \operatorname{Na_2CO_3} \longrightarrow \operatorname{AgCl} + \operatorname{HNO_3} \\ \operatorname{(E)} \\ \operatorname{(D)} \\ \operatorname{AgCl} + \operatorname{2NH_4OH} \longrightarrow \operatorname{Ag}(\operatorname{NH_3})_2\operatorname{Cl} + 2\operatorname{H_2O} \\ \operatorname{(E)} \\ \operatorname{(E)} \\ \operatorname{(Colourless\ solution} \\ \end{array}$$

- (A) = Silver glance, Ag<sub>2</sub>S
- (B) = Sodium argentocyanide, NaAg(CN)<sub>2</sub>
- (C) = Sodium sulphate, Na<sub>2</sub>SO<sub>4</sub>
- (D) = Silver metal, Ag
- (E) = Silver chloride, AgCl
- (F) = Diamminosilver (I) chloride,  $Ag(NH_3)_2Cl$

**Example 12.** (i) A black coloured compound (B) is formed on passing hydrogen sulphide through the solution of a compound (A) in  $NH_4OH$ .

- (ii) (B) on treatment with HCl and potassium chlorate gives A.
- (iii) (A) on treatment with potassium cyanide gives a buff coloured precipitate which dissolves in excess of this reagent forming a compound (C).
- (iv) The compound (C) is changed into a compound (D) when its aqueous solution is boiled.
- (v) The solution of (A) was treated with excess of sodium bicarbonate and then with bromine water. On cooling and shaking for sometime, a green coloured compound (E) is formed. No change is observed on heating. Identify (A) to (E) and give chemical equations at steps (i) to (v). [Roorkee 1996]

#### **Solution:**

The formation of a black coloured precipitate on passing  $H_2S$  in alkaline medium indicates that the salt is either of cobalt or nickel. However, the reaction (iii) suggests that (A) is a cobalt salt (CoCl<sub>2</sub>). This is confirmed by the following reactions:

(i) 
$$CoCl_2+H_2S+2NH_4OH \longrightarrow CoS + 2NH_4Cl + 2H_2O$$
(B)
(B)

(ii) 
$$CoS + 2HCl + [O] \longrightarrow CoCl_2 + H_2O$$
  
(B) From  $KClO_3$  (A)

(iii) 
$$CoCl_2 + 2KCN \longrightarrow 2KCl + Co(CN)_2$$
 $Buff coloured$ 
 $Co(CN)_2 + 4KCN \longrightarrow K_4Co(CN)_6$ 
(iv)  $2K_4Co(CN)_6 + H_2O + [O] \longrightarrow 2K_3Fe(CN)_6 + 2KOH$ 
 $CO \longrightarrow From \ air \ (D)$ 
Pot. cobaltocyanide Pot. cobalticyanide
(v)  $CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl$ 
 $Co(HCO_3)_2 + 4NaHCO_3 \longrightarrow Na_4Co(CO_3)_3 + 3CO_2 + 3H_2O$ 
 $Br_2 + H_2O \longrightarrow 2HBr + [O]$ 
 $2Na_4Co(CO_3)_3 + H_2O + [O] \longrightarrow 2Na_3Co(CO_3)_3 + 2NaOH$ 

(E) is stable towards heat.

Example 13. When the ore haematite is burnt in air with coke around 2000°C along with lime, the process not only produces steel but also produces a silicate slag that is useful in making building materials such as cement. Discuss the same and show through balanced chemical equations. [I.I.T. 1998] [Hint: Haematite (Fe<sub>2</sub>O<sub>3</sub>) on burning with coke and lime at 2000°C results in the following:

Green coloured solution

$$\begin{array}{c} C + O_2 \longrightarrow CO_2 \\ CO_2 + C \longrightarrow 2CO \\ \end{array}$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2 \\ Steel \\ SiO_2 + CaO \longrightarrow CaSiO_3 \\ Lime & Slag \end{array}$$

(used as a building material)]

Example 14. An aqueous solution containing 1 mole of  $HgI_2$  and 2 moles of NaI is orange in colour. On addition of excess of NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl. Explain with equations. [I.I.T. 1999]

[Hint: HgI<sub>2</sub> is sparingly soluble in water and gives orange solution. On addition of excess of NaI, the colourless soluble complex Na<sub>2</sub>HgI<sub>4</sub> is formed.

$$HgI_2 + 2NaI \longrightarrow Na_2HgI_4$$

The complex reacts with NaOCl with formation of again HgI<sub>2</sub>, *i.e.*, orange colour is restored.

 $3 \text{Na}_2 \text{HgI}_5 + 2 \text{NaOCl} + 2 \text{H}_2 \text{O} \longrightarrow 3 \text{HgI}_2 + 2 \text{NaCl} + 4 \text{NaOH} + 2 \text{NaI}_3]$ 

#### Example 15. Explain:

- (i) Why are Sm<sup>2+</sup>, Eu<sup>2+</sup> and Yb<sup>2+</sup> good reducing agents?
- (ii) Can lanthanum (Z = 57) exhibit +4 oxidation state?
- (iii) Why are +3 oxidation state of gadolinium (Z = 64) and lutetium (Z = 91) especially stable?
  - (iv) Why do Zr and Hf exhibit similar properties?

#### **Solution:**

(i) The most stable oxidation state of lanthanides is +3. Hence, ions in +2 state tend to change to +3 oxidation state by loss of electron and act as reducing agents.

- (ii)  $La^{3+}$  has a stable configuration of an inert gas  $[(Xe)5d^06s^0]$ , *i.e.*, xenon (54—2, 8, 18, 18, 8). To obtain +4 oxidation state, the stable configuration is to be disturbed which is not possible under ordinary conditions and hence  $La^{4+}$  does not exist.
- (iii) This is because gadolinium in +3 state has half filled 4f-subshell  $(4f^7)$  and lutetium in +3 state has completely filled 4f-subshell which are very stable configurations.
- (iv) Due to lanthanide contraction, the atomic radii of both Zr and Hf are same. Hence, their properties are similar.

**Example 16.** Why is dilute sulphuric acid and not dilute HCl or HNO<sub>3</sub> used to acidify a permanganate solution in volumetric analysis?

#### **Solution:**

Volumetric titrations involving potassium permanganate solution are carried out only in presence of dilute H<sub>2</sub>SO<sub>4</sub> but not in presence of dilute HCl or dilute HNO<sub>3</sub>. This is because oxygen produced from KMnO<sub>4</sub> + dil. H<sub>2</sub>SO<sub>4</sub> is used only for oxidising the reducing agent. Moreover, H<sub>2</sub>SO<sub>4</sub> does not give any oxygen of its own to oxidise the reducing agent.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[\Theta] -$$

Reducing agent + [O] → Oxidised product

In case HCl is used, the oxygen produced from KMnO<sub>4</sub> is partly used upto oxidise HCl and Cl<sub>2</sub> is produced.

$$2KMnO_4 \longrightarrow K_2O + 2MnO + 5[O]$$

$$K_2O + 2HC1 \longrightarrow 2KC1 + H_2O$$

$$[MnO + 2HC1 \longrightarrow MnCl_2 + H_2O] \times 2$$

$$[2HCl + [O] \longrightarrow H_2O + Cl_2] \times 5$$

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

In case HNO<sub>3</sub> is used, it itself acts as an oxidising agent and partly oxidises the reducing agent.

**Example 17.** What is the equivalent mass of  $KMnO_4$  when it acts as an oxidising agent in acidic medium (molecular mass  $KMnO_4 = 158$ )?

#### Solution:

Oxidising action of KMnO<sub>4</sub> acidic medium is represented as:

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
  
 $2 \times 158 \text{ g}$   $5 \times 16 = 80 \text{ g}$ 

Eq. mass of KMnO<sub>4</sub> = 
$$\frac{2 \times 158}{80} \times 8 = 31.6$$

or Eq. mass of KMnO<sub>4</sub>

 $= \frac{\text{Molecular mass}}{\text{Number of electrons gained per molecule}}$  $= \frac{158}{5} = 31.6$ 

or 
$$MnO_4^- \longrightarrow Mn^{2+}$$
  
Oxidation state  $+7 \longrightarrow +2$ 

Eq. mass of KMnO<sub>4</sub>

$$= \frac{\text{Molecular mass}}{\text{Change in oxidation state per molecule}}$$
$$= \frac{158}{5} = 31.6$$

**Example 18.** Explain the following giving suitable reason:

- (i) Yellow coloured aqueous solution of sodium chromate changes to orange red when CO<sub>2</sub> under pressure is passed.
- (ii) Green solution of potassium manganate,  $K_2MnO_4$ , turns purple when  $CO_2$  is circulated.

#### Solution:

(i) Yellow coloured aqueous solution of sodium chromate changes to orange red on passing CO<sub>2</sub> as H<sup>+</sup> ions are formed which are responsible for conversion of chromate into dichromate.

$$CO_2 + H_2O \Longrightarrow H^+ + HCO_3^-$$

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$
Yellow Orange red

(ii) CO<sub>2</sub> gives H<sup>+</sup> ions which are responsible for conversion of manganate (green) to permanganate (purple).

$$CO_2 + H_2O \Longrightarrow H^+ + HCO_3^-$$
  
 $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$   
Green Purple

**Example 19.** Assign reason for each of the following:

- (i)  $Ce^{3+}$  can be easily oxidised to  $Ce^{4+}$ .
- (ii)  $E^o$  for  $Mn^{3+}/Mn^{2+}$  couple is more positive than for  $Fe^{3+}/Fe^{2+}$  couple.
  - (iii) Lu(OH)3 is a weaker base than La(OH)3.

#### **Solution:**

(i)  $Ce^{3+}$  has the configuration  $4f^15d^06s^0$ . It can easily lose an electron to acquire more stable configuration  $(4f^05d^06s^0, i.e., configuration of an inert gas, xenon 2, 8, 18, 18, 8), i.e., <math>Ce^{3+}$  can be easily oxidised to  $Ce^{4+}$ .

$$Ce^{3+} \longrightarrow Ce^{4+} + e^{-1}$$

(ii)  $E^{\circ}$  for  $Mn^{3+}/Mn^{2+}$  couple is more positive than for  $Fe^{3+}/Fe^{2+}$  couple because  $Mn^{2+}$  state is more stable than  $Mn^{3+}$  state. Thus, the reduction is spontaneous.

$$Mn^{3+}(3d^4,4s^0) + e \longrightarrow Mn^{2+}(3d^5,4s^0)$$

For Fe<sup>3+</sup>/Fe<sup>2+</sup> couple, Fe<sup>3+</sup>( $3d^5$ , $4s^0$ ) is more stable than Fe<sup>2+</sup>( $3d^6$ , $4s^0$ ). Thus, the reduction is not spontaneous.

(iii) In the lanthanide series, the size of the  $M^{3+}$  ion decreases from  $La^{3+}$  to  $Lu^{3+}$ . Thus, the covalent nature of  $Lu(OH)_3$  increases (Fajan's rule). Hence,  $Lu(OH)_3$  is weaker than  $La(OH)_3$ .

**Example 20.** Transition metals of 3d-series do not react readily with dilute acids to liberate hydrogen although they have high negative reduction potential values. Explain.

#### Solution:

Most of the transition metals have the tendency to form a protective layer of their oxides on the surface. This oxide layer is somewhat inert and does not permit the metals to react with dilute acids to liberate hydrogen.

**Example 21.** The atomic radii of the elements in a transition series do not vary much while they do vary in the case of s and p-block elements. Explain.

#### **Solution:**

There are operating two effects namely nuclear charge effect and screening effect which oppose each other. Due to increase in nuclear charge from member to member in a transition series, the atomic radii tend to decrease. At the same time, the addition of extra electrons one by one to (n-1)d-orbitals provides the screening effect. As the number of d electrons increases, the screening effect increases and this tends to increase size. Due to these opposing tendencies, there is a very small change in the atomic radii in a transition series. In s and p-block elements, the extra electron is added to same s or p-subshell-which does not exert screening effect and hence, the atomic radii decreases considerably in a period due to increase in nuclear charge.

**Example 22.** The second and third members in each group of the transition elements have similar atomic radii. Explain.

#### Solution:

This is due to lanthanide contraction by the members of 4f-series which occupy a position between lanthanum (Z = 57, a first member of third transition series) and hafnium (Z = 72, second member of 3rd transition series).

The pairs of elements such as Zr-Hf, Nb-Ta, Mo-W, etc., possess nearly the same atomic radii and almost the same properties.

**Example 23.** (a) Chromium is a typical hard metal while mercury is a liquid. Explain.

- (b) The melting and boiling points of Zn, Cd and Hg are low. Why?
- (c) Though copper, silver and gold have completely filled sets of d-orbitals, yet they are considered as transition metals. Why?

#### **Solution:**

- (a) In chromium, the interatomic bonding is very strong due to presence of five unpaired electrons in 3d-subshell  $(3d^54s^1)$ . Therefore, it is a hard metal. In mercury, on the contrary, the 3d-subshell is filled to maximum capacity  $(5d^{10}6s^2)$ , i.e., these electrons are not available for interatomic bonding and thus, bonding is very weak in mercury. Therefore, mercury is a liquid at room temperature.
- (b) In Zn, Cd and Hg, the (n-1) *d*-orbitals are filled to their maximum capacity. These *d*-electrons do not take part in metallic bonding. Thus, metallic bonding is weak in Zn, Cd and Hg. That is why, they have low melting and boiling points.
- (c) Copper, silver and gold in their common oxidation states have partially filled (n-1) *d*-orbitals.

$$Cu^{2+}(3d^9)$$
;  $Ag^{2+}(4d^9)$ ;  $Au^{3+}(5d^8)$ 

**Example 24.** (a) Of the ions  $Ag^+$ ,  $Co^{2+}$  and  $Ti^{4+}$  which ones will be coloured in aqueous solution?

(b) If each one of the above ionic species is in turn placed in a magnetic field, how will it respond and why?

#### **Solution:**

- (a) The ionic species which possesses unpaired electron or electrons in (n-1) d-subshell will show colour. Of the ions  $Ag^+(4d^{10})$ ,  $Co^{2+}(3d^7$ —three unpaired electrons) and  $Ti^{4+}(3d^0)$ ,  $Co^{2+}$  will be coloured as it contains three unpaired electrons and  $Ag^+$  and  $Ti^{4+}$  will be colourless.
- (b) When placed in magnetic field, Co<sup>2+</sup> will be attracted because it is paramagnetic due to unpaired electrons. Ag<sup>+</sup> and Ti<sup>4+</sup> ions will be repelled by the magnetic field as they are diamagnetic due to presence of paired orbitals.

**Example 25.** Give examples and suggest reasons for the following features of the transition metal chemistry:

- (i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
- (ii) A transition metal exhibits highest oxidation state in oxides and fluorides.
- (iii) The highest oxidation state is exhibited in oxoanions of a metal.

#### **Solution:**

- (i) In case a metal forms a number of oxides, the acidic strength increases with the increase in oxidation state of the metal, *i.e.*, acidic strength increases with the increase in percentage of oxygen in the oxide. For example, MnO is a basic oxide while  $Mn_2O_7$  is an acidic oxide.
- (ii) A metal exhibits higher oxidation states in oxides and fluorides as oxygen and fluorine are highly electronegative elements and small in size, *i.e.*, act as strong oxidising agents. For example, chromium shows an oxidation state of +6 in  $CrF_6$  and osmium shows an oxidation state of +8 in  $OsO_4$ .
- (iii) This is also because of high electronegativity of oxygen. For example, chromium shows oxidation state of +6 in  ${\rm Cr_2O_7^{2-}}$  and manganese shows oxidation state of +7 in  ${\rm MnO_4^{-}}$ .

**Example 26.** (a) Actinide contraction is greater from element to element than lanthanide contraction. Why?

(b) The outer electronic configuration of two members of the lanthanide series are as follows:

$$4f^{1}5d^{1}6s^{2}$$
 and  $4f^{7}5d^{0}6s^{2}$ 

What are their atomic numbers? Predict the oxidation states exhibited by these elements in their compounds.

#### **Solution:**

- (a) This is due to poor shielding by 5f electrons in the actinides than that of 4f electrons in the lanthanides.
- (b) Complete E.C. of 1st element : [Xe]  $4f^15d^16s^2 = 58$ , *i.e.*, the element is cerium.

Complete E.C. of 2nd element : [Xe]  $4f^75d^06s^2 = 63$ , *i.e.*, the element is europium.

The expected oxidation states of 1st element = +3, and +4 and of 2nd element = +2, +3.

**Example 27.** Which is the most common oxidation state of lanthanides and how is it formed? Give its configuration. Solution:

The most common oxidation state of lanthanides is +3. This oxidation state of the lanthanide ions arises due to the loss of two 6s electrons and the lone 5d electron, if present from the atom of the elements. If no electron is present in the 5d orbital, than one of electrons from 4f shell is lost. The lanthanides in this state have the general configuration [Xe]  $4f^{1-14}$ .



# **SUMMARY AND IMPORTANT POINTS TO REMEMBER**



1. The elements belonging to groups 3 to 12 of the extended form of the periodic table are called d-block elements. They are present between s-block and p-block elements and belong to 4th, 5th, 6th and 7th periods of periodic table. They are also called transition elements (elements having incomplete (n-1)d-orbitals in their atoms or in their simple ions). Their general electronic configuration is:

$$(n-1)d^{1-10}ns^{0, 1 \text{ or } 2}$$

All transition elements are d-block elements but all d-block elements are not transition metals. For example, the elements of group 12, namely Zn, Cd, Hg and Uub, though belong to d-block but are not considered as transition metals because they contain completely filled (n-1)d-orbitals.

2. There are four transition series which involve the filling of (n-1)d-subshell. Each series consists ten elements. Each series starts from a member of third group and ends with a member of group 12.

First series (3*d*-series) Sc 
$$(3d^1,4s^2)$$
 — Zn  $(3d^{10},4s^2)$  (21) (30)  
Second series (4*d*-series) Y  $(4d^1,5s^2)$  — Cd  $(4d^{10},5s^2)$  (39) (48)  
Third series (5*d*-series) La  $(5d^1,6s^2)$  — Hg  $(5d^{10},6s^2)$  (57) (80)  
Fourth series (6*d*-series) Ac  $(6d^1,7s^2)$  — Uub  $(6d^{10},7s^2)$  (89) (112)

Certain elements show exceptional electronic configuration. In the first transition series Cr  $(3d^5,4s^1)$  and Cu  $(3d^{10},4s^1)$  have exceptional configuration.

The elements of first transition series are:
 Sc (21), Ti (22), V (23), Cr (24), Mn (25), Fe (26),
 Co (27), Ni (28), Cu (29) and Zn (30).

4. All the transition elements are metals. Iron is the most

abundant transition metal in the earth's crust. Technetium and all the members of fourth transition series are radioactive. Technetium is the first synthetic element. The elements after uranium are termed transuranic elements. These elements have been obtained artificially by nuclear transmutation. Transition elements have high density, hardness, high tensile strength, malleability, ductility, high thermal and electrical conductivity, high energy of atomisation, high melting and boiling points. Larger the number of unpaired electrons, stronger is the metallic bond and hence higher is the energy of atomisation and the melting point. That is why melting points increase in each series up to the fourth member, i.e., Cr, Mo and W (W—highest melting point 3410°C). However, the melting point of manganese in 3d-series is lower than its neighbours. This is due to stable configuration of manganese  $(3d^5, 4s^2)$ , i.e., metallic bonding is less. Among the transition metals, the lightest is Sc (density 3.0 g cm<sup>-3</sup>) and heaviest osmium (22.59 g cm<sup>-3</sup>) and iridium (22.61 g cm<sup>-3</sup>). Hg is known in liquid form under ordinary conditions.

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- 5. Generally, the atomic radii of *d*-block elements in a series decrease with increase in atomic number but the decrease in atomic size is small after midway. In the first series, the atomic radii decrease upto Cr but after that it remains almost the same. The atomic radii of second and third transition series in the same vertical columns are almost the same. This is due to lanthanide contraction. The atomic radii of the pairs such as Zr-Hf, Nb-Ta, Mo-W, Ag-Au, etc., are almost same.
- 6. The ionisation energy gradually increases with increase in atomic number along a given transition series. The ionisation energies of 3d and 4d elements are irregular. The first ionisation energy of 5d elements is higher than 3d and 4d elements belonging to same group due to lanthanide contraction.
- 7. Transition metals show variable oxidation states (except first and last member of the series). The most common oxidation state of the first transition series is +2 except scandium. The maximum oxidation state increases with atomic number upto manganese in the first transition series. This is due to the involvement of 4s electrons and unpaired electrons of 3d-subshell. Manganese  $(3d^54s^2)$  shows maximum oxidation state of +7. Lower states are ionic while higher states are covalent.

The highest oxidation state shown by transition metal is +8 (by Ru and Os). Ions with the metal in a high oxidation state tend to be good oxidising agents ( $Cr_2O_7^{2-}$ ,  $MnO_4^-$ ) and ions with the metal in low oxidation state are good reducing agents ( $V^{2+}$ ,  $Cr^{2+}$ ).

- 8. Most of the transition metals and their compounds exhibit paramagnetism. Substances containing unpaired electrons are paramagnetic. Those containing no unpaired electron are diamagnetic. (Zn, Cd, Hg, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Cu<sup>+</sup>, Sc<sup>3+</sup>, Ti<sup>4+</sup>, V<sup>5+</sup>, etc., are diamagnetic.) Magnetic moment is given as  $\mu = \sqrt{n(n+2)}$  B.M., where n = number of unpaired electrons. In the first transition series Cr has maximum paramagnetism and amongst ions Mn<sup>2+</sup> has maximum magnetic moment.
- 9. Most of the transition metal compounds (ionic as well as covalent) are coloured both in solid state and in aqueous solution. Colour is due to the presence of incomplete d-subshell, i.e., there is d-d transition. The ions with  $(n-1)d^0$  or  $(n-1)d^{10}$  configuration are colourless.  $Sc^{3+}$ ,  $Te^{4+}$ ,  $Cu^+$ ,  $Zn^{2+}$ , etc., are colourless because they have either  $3d^0$  or  $3d^{10}$  configuration. The following colours are observed for the common ions.

Ti<sup>3+</sup> V<sup>3+</sup> Mn<sup>3+</sup> Fe<sup>3+</sup> Fe<sup>2+</sup> Cu<sup>2+</sup> Co<sup>2+</sup> Ni<sup>2+</sup> Purple Green Violet Yellow Green Blue Pink Green

- 10. Transition metals have the tendency to form complex compounds, interstitial compounds and alloys. They and their compounds act as good catalysts.
- 11. Iron, cobalt and nickel are termed ferrous metals. Copper, silver and gold are called coinage metals. Zinc, cadmium and

mercury are called zinc metals. Principal ores of iron, copper, silver, zinc and mercury are:

Iron		Copper	,
Haematite	Fe <sub>2</sub> O <sub>3</sub>	Copper glance	Cu <sub>2</sub> S
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	Copper pyrites or Chalcopyrites	CuFeS <sub>2</sub>
Limonite	Fe <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O	Malachite	Cu(OH)2·CuCO3
Siderite	FeCO <sub>3</sub>	Azurite	Cu(OH) <sub>2</sub> ·2CuCO <sub>3</sub>
Iron pyrite	FeS <sub>2</sub>	Cuprite	Cu <sub>2</sub> O
Silver		Zinc	•
Argentite or silver glance	Ag <sub>2</sub> S	Zinc blende	ZnS
Hom silver	AgCl	Calamine	$ZnCO_3$
	_	Zincite	ZnO
Mercury			
Cinnabar	HgS		

- 12. There are three commercial varieties of iron:
  - (i) Pig iron or cast iron: This is the most impure form. It contains about 2-5% carbon along with varying amounts of Mn, Si, S, P, etc. It is hard and brittle. It cannot be welded. It is used for casting purposes.
  - (ii) Wrought iron: It is the purest form. It contains not more than 0.5% impurities including carbon. It is soft, malleable and ductile. It can be welded. It can be easily magnetised.
  - (iii) Steel: The carbon content is between 0.5 to 1.5%. It contains small amounts of other metals such as Cr, Ni, Mn, etc.
- **13.** Cast iron or pig iron is usually extracted from the oxide ore. It involves the following steps:
  - (i) Concentration by gravity process; (ii) Calcination in reverberatory furnace; (iii) Smelting in blast furnace. The calcined ore is mixed with coke and limestone and smelted in the blast furnace where CO produced as a result of combustion of coke reduces  $Fe_2O_3$  into Fe.

$$\begin{split} \text{Fe}_2\text{O}_3 + \text{CO} &\longrightarrow 2\text{FeO} + \text{CO}_2 \\ \text{FeO} + \text{CO} &\longrightarrow \text{Fe} + \text{CO}_2 \\ \text{CaCO}_3 &\longrightarrow \text{CaO} + \text{CO}_2 \\ \text{CaO} + \text{SiO}_2 &\longrightarrow \text{CaSiO}_3 \\ \text{Slag} \end{split}$$

- 14. Steel is manufactured from cast iron or pig iron by Bessemer process, open hearth process or electric process. Spiegeleisen—an alloy of Fe, Mn and C is added during manufacture. Steel is given heat treatment in order to impart special properties.
  - (i) Annealing: It involves heating of steel much below red heat and then cooled slowly. It makes steel soft.
  - (ii) Quenching: It involves heating of steel to red heat followed by sudden cooling by plunging into water or oil. It makes steel hard and brittle.
  - (iii) Tempering: It involves heating of steel which has already been quenched to a temperature 230-300°C and then allowed to cool slowly. It makes steel hard but brittleness disappears.

Some special steels are:

(i) Stainless steel (Fe, Cr, Ni, C). It is resistant to corrosion

- and is used for making utensils, cutlery and ornamental pieces.
- (ii) Invar (Fe, Ni). It has small coefficient of expansion and is used for making metre rods, pendulum rods and springs for watches.
- (iii) Manganese steel (Fe, Mn, C). It is very hard. It is used for making rock drills, almirah, etc.
- (iv) Tungsten steel (Fe, W, C). It is hard and is used for making high speed cutting tools.
- (v) Alnico (Fe, Al, Ni, Co). It is highly magnetic and is used for making permanent magnets.
- 15. Copper is extracted from chalcopyrites. The ore is concentrated by froth floatation process, roasted in reverberatory furnace and then smelted in a blast furnace when molten 'matte' containing Cu<sub>2</sub>S + FeS (little) is obtained. It is transferred to Bessemer converter and heated with a blast of hot air, when blister copper is obtained.

$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$

Blister copper contains 96–98% copper along with small amounts of Ag, Au, Ni, Zn, Pb, Sn, etc. It is further purified by poling process and electrolytic process.

Copper is used for making electrical wires, electroplating, coins and many useful alloys such as brass (Cu and Zn), bronze (Cu and Sn), german silver (Cu, Zn and Ni), constantan (Cu and Ni), rolled gold (Cu and Al), etc.

16. Silver is extracted from argentite. It is concentrated by froth floatation process. The concentrated ore is ground to fine powder. This is treated with dilute solution (0.4 to 0.6%) of sodium cyanide and a current of air is circulated. Silver present in the ore dissolves.

$$Ag_2S + 4NaCN \Longrightarrow 2NaAg(CN)_2 + Na_2S$$

$$4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$$

Silver is precipitated from the solution by addition of zinc powder.

$$2NaAg(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2Ag$$

The precipitated silver is dried and fused with KNO<sub>3</sub> in a crucible. Liquid silver on cooling appears as a compact mass. The main impurities are lead, copper and gold. These are removed by cupellation and electrolytic processes. Silver is used, for making coins, ornaments, silverware and in electroplating. Silver salts are used in photography, silvering of mirrors and for making marking inks and medicine.

17. Zinc is extracted either from zinc blende or calamine. When zinc blende is used the powdered ore is concentrated by froth floatation process. In case of calamine, the ore is concentrated by gravity process. The concentrated ore is heated in excess of oxygen at about 900°C. Zinc sulphide is oxidised to zinc oxide.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

Reduction of oxide is done by carbon.

$$ZnO + C \longrightarrow Zn + CO$$
,  $ZnO + CO \longrightarrow Zn + CO_2$ 

Zinc is also recovered by electrolytic process. The roasted ore is dissolved in dilute sulphuric acid. The solution is freed from iron, aluminium and silica, etc. The solution is then electrolysed by using a sheet of pure Al as cathode and pure lead plate as anode. The zinc is removed from cathode by melting. The zinc obtained is 99.95% pure.

The impure zinc obtained by reduction process is known as **spelter.** Granulated zinc is made by melting the metal in a crucible and pouring the drops in water. Zinc dust is made by melting zinc and then atomising it with a blast of air. Zinc is used in the manufacture of various important alloys such as brass, german silver, etc. The most important use of zinc is for galvanising iron. It is also used for extraction of Ag and Au, as a reducing agent in laboratory and zinc rods in making electric batteries.

**18.** Mercury is extracted from cinnabar. It is concentrated by froth floatation process. The concentrated ore is then roasted in excess of air when mercury is obtained.

$$HgS + O_2 \longrightarrow Hg + SO_2$$

The mercury is refined by first passing it through dilute HNO<sub>3</sub> and then distilled. Mercury forms alloys (amalgams) with all metals except Fe and Pt. Hg is used in thermometers, manometers and barometers.

(i) Copper sulphate (CuSO<sub>4</sub>·5H<sub>2</sub>O) is called blue vitriol. It
is prepared by dissolving cupric oxide, cupric hydroxide
or copper carbonate in dilute H<sub>2</sub>SO<sub>4</sub>.

In  $CuSO_4.5H_2O$ , the four water molecules are coordinated to control  $Cu^{2+}$  ion while fifth one is attached to  $SO_4^{2-}$  ion by H-bonding.

With KI, it gives white Cu<sub>2</sub>I<sub>2</sub> and free iodine.

$$[2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2]$$

With excess of NH<sub>4</sub>OH, CuSO<sub>4</sub> gives deep blue solution due to complex formation.

$$CuSO_4 + 4NH_4OH \longrightarrow Cu(NH_3)_4SO_4 + 4H_2O$$

A mixture of CuSO<sub>4</sub> and Ca(OH)<sub>2</sub> is used as a fungicide under the name of **Bordeaux mixture**.

- (ii) Silver nitrate (AgNO<sub>3</sub>) is called **lunar caustic.** It is obtained by dissolving silver in dilute nitric acid. On coming in contact with organic matter like skin or cloth it is reduced to silver giving a black stain. It gives different coloured precipitates with acidic radicals such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CrO<sub>4</sub><sup>2</sup>, S<sup>2</sup>-, S<sub>2</sub>O<sub>3</sub><sup>2</sup>-, PO<sub>4</sub><sup>3</sup>-, etc.
  - It is used for making silver halides, as a laboratory reagent, silvering mirrors and for making marking ink.
- (iii) Out of AgCl, AgBr and AgI, AgBr is most sensitive to light and is used in photography.
- (iv) Hg forms two chlorides. Mercury (I) chloride, i.e., mercurous chloride (Hg<sub>2</sub>Cl<sub>2</sub>) is also called calomel. It is nonpoisonous. It turns black when treated with ammonia due to deposition of Hg. The oxidation state of Hg is +1 but valency is 2, e.g., in Hg<sub>2</sub><sup>2+</sup> (—Hg—Hg—) two atoms are joined together by a covalent bond. It is used for making calomel electrode and as a purgative in medicine.

Mercury(II) chloride, *i.e.*, mercuric chloride (HgCl<sub>2</sub>) is also called **corrosive sublimate.** It is highly poisonous (corrosive) and undergoes sublimation. Its antidote is

the white of an egg. It is less soluble in cold water but soluble in hot water and in organic solvents. It is a covalent compound. It is reduced by SnCl<sub>2</sub> and copper. Its very dilute solution (0.1%) is used as antiseptic.

- (v) HgI<sub>2</sub> dissolves in excess of KI to form K<sub>2</sub>HgI<sub>4</sub>. An alkaline solution of K<sub>2</sub>HgI<sub>4</sub> is called Nessler's reagent. It is used for the test of NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup> ion.
- (vi) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is prepared from the chromite ore (FeO·Cr<sub>2</sub>O<sub>3</sub>). The finely powdered ore is mixed with sodium carbonate and the mixture is fused in reverberatory furnace in excess of air. The roasted mass is extracted with water and the solution is treated with conc. H<sub>2</sub>SO<sub>4</sub>·Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O being less soluble crystallises our and is filtered. Hot solution of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is treated with calculated amount of KCl when K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> crystals are obtained.

$$4\text{FeO}\cdot\text{Cr}_2\text{O}_3 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow$$

$$8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$
Soluble Insoluble ==
$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

It is an orange crystalline compound. It decomposes on heating to give  $K_2CrO_4$ ,  $Cr_2O_3$  and  $O_2$ . Its acidic solution contains dichromate ions while alkaline solution contains chromate ions. It is a strong oxidising agent. Acidified solution is used as a primary standard in volumetric analysis for the estimation of reducing agents such as ferrous sulphate, oxalic acid, etc. On heating with a chloride (NaCl) and conc.  $H_2SO_4$ , red vapours of  $CrO_2Cl_2$  (chromyl chloride) are evolved. Its equivalent mass in acidic medium is mol. mass/6 = 49.

finely powdered ore is fused with KOH or K<sub>2</sub>CO<sub>3</sub> in presence of air or oxidising agent when K<sub>2</sub>MnO<sub>4</sub> (manganate) is formed. It is oxidised chemically by using H<sub>2</sub>SO<sub>4</sub>, CO<sub>2</sub> or Cl<sub>2</sub> or electrolytically.

It is a deep purple crystalline compound, moderately soluble in water. It decomposes when heated giving O<sub>2</sub>. It acts as a strong oxidising agent in neutral, alkaline and acidic media. The acidified KMnO<sub>4</sub> (dil. H<sub>2</sub>SO<sub>4</sub>) is used as a volumetric reagent. It is not a primary standard, *i.e.*, it is first standardised and then used. Its equivalent mass in acidic medium is mol. mass/5 = 31.6. Alkaline KMnO<sub>4</sub> solution is called **Baeyer's reagent** used in organic analysis. It has tetrahedral structure.

(vii) KMnO<sub>4</sub> is prepared from pyrolusite ore (MnO<sub>2</sub>). The

**20.** The *f*-block elements (inner transition elements) are placed outside the periodic table. Their general configuration is :

$$(n-2)f^{1-14}(n-1)d^{0,1}ns^2$$

There are two series:

- (a) **4f-series:** 4f-orbitals are gradually filled up. These are 14 elements from Ce (58) to Lu(71) and are called lanthanides as these show similarities with La(57).
- **(b) 5***f***-series:** 5*f*-orbitals are gradually filled up. These are also 14 elements from Th (90) to Lr (103) and are called **actinides** as these show similarities with actinium,

Ac (89). These are radioactive elements. Most of these are man-made.

- 21. There is gradual decrease in the atomic and ionic sizes of these metals along the series. These are called lanthanide contraction and actinide contractions. Lanthanide contraction is responsible for various changes in chemical properties of the elements succeeding them.
- 22. All the lanthanides are rather soft white metals. They react easily with water to give solutions giving +3 ions. The principal oxidation state is +3 although +4, +2 oxidation states are also exhibited. Those having +2 (i.e., Sm<sup>2+</sup>, Eu<sup>2+</sup> and Yb<sup>2+</sup>) change to +3, and act as reducing agents. Those having +4 tend to change to +3 and act as oxidising agents. The maximum oxidation state shown by actinides is +7. U, Np and Pu show oxidation state of +6. However, all the actinides also show +3 oxidation state.
- 23. Paramagnetism is shown by the positive ions of lanthanides except  $La^{3+}(4f^0)$  and  $Lu^{3+}(4f^{14})$ . Most of the trivalent lanthanide ions are coloured. This is due to f-f transition. Actinide cations are also generally coloured. The cations having  $5f^0$  or  $5f^7$  or  $5f^{14}$  configuration are colourless.
- 24. La(OH)<sub>3</sub> is most basic while Lu(OH)<sub>3</sub> is least basic.
- 25. The inertness exhibited by certain metals under conditions when chemical activity is to be expected is called passivity. Iron is rendered passive by oxidising agents like conc. HNO<sub>3</sub>, conc. H<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub>, chromic acid, etc. The passivity of iron is believed to be due to formation of an extremely thin film of oxide on the surface. Passive iron can be made active by scratching or removing oxide film chemically.
- 26. There are many compounds of transition metals which are used as catalysts. For example:

Adam's catalyst

- Pt/PtO

Brown's catalyst

Nickel boride

Zeigler-Natta catalyst

- TiCl<sub>4</sub> + (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al

Wilkinson's catalyst

— [Ph<sub>3</sub>P]RhCl

27. There are many compounds of transition elements which are used as reagents in laboratory or industry. For example,

Baeyer's reagent

Dilute alkaline soln. of KMnO<sub>4</sub>

Tollen's reagent

AgNO<sub>3</sub> soln. + NaOH soln.

+ NH₄OH

Schweitzer's reagent ---

[Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>

Nessler's reagent

Alk. soln. of K2HgI4

Benedict's solution

CuSO<sub>4</sub> soln. + sod. citrate

+ Na<sub>2</sub>CO<sub>3</sub>

Fehling's solution

CuSO<sub>4</sub> soln. + sodium potassium

tartrate

Fenton's reagent

 $FeSO_4 + H_2O_2$ 

Etard's reagent

CrO<sub>2</sub>Cl<sub>2</sub>

Bordeaux mixture

— CuSO<sub>4</sub> soln. + lime

Lucas reagent

— Conc. HCl + anhydrous ZnCl<sub>2</sub>

Barfoed's reagent — Cu(CH<sub>3</sub>COO)<sub>2</sub>+CH<sub>3</sub>COOH

28. Some of the substances having compounds of transition metals are given special names.

Paris green — Cu(CH<sub>3</sub>COO)<sub>2</sub>·3Cu(AsO<sub>2</sub>)<sub>2</sub>

Rinnmann's green ZnO·CoO or CoZnO<sub>2</sub> (Cobalt zincate)

Verdigris — Cu(CH<sub>3</sub>COO)<sub>2</sub>·Cu(OH)<sub>2</sub>

Fulminating gold

Calomel — Hg<sub>2</sub>Cl<sub>2</sub> Corrosive sublimate — HgCl<sub>2</sub> Lunar caustic — AgNO₃ Philospher's wool - ZnO

or pompholyx

Blue vitriol — CuSO<sub>4</sub>·5H<sub>2</sub>O (Nila Thotha) Green vitriol — FeSO<sub>4</sub>·7H<sub>2</sub>O (Hara kasis)

Horn silver - AgCl

Mohr's salt — FeSO<sub>4</sub>·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O

Prussian blue - Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub> White vitriol — ZnSO₄·7H₂O

Vermilion --- HgS

Purple of cassius -- Colloidal gold solution

Fool's gold — FeS<sub>2</sub> or CuFeS<sub>2</sub> Titanox - TiO<sub>2</sub> + BaSO<sub>4</sub> --- ZnS + BaSO<sub>4</sub> Lithophone

Vaska's compound — Trans IrCl (CO) (PPh<sub>3</sub>)<sub>2</sub>

- 29. Finely reduced form of platinum in the form of velvety black powder is called platinum black.
- 30. Titanium has been called 'The wonder metal' because of its useful properties. It is very hard, very light and has high melting point.
- 31. Mischmetal, an alloy which contains rare earth elements (94– 95%), iron (5%) and traces of sulphur, carbon, silicon, calcium and aluminium. It is pyrophoric and is used in cigarette and gas lighters, tracer bullets and shells. The main rare earth elements present in this alloy are cerium (≈ 40%), lanthanum and neodymium ( $\approx 44\%$ ).

An alloy containing magnesium and about 3% mischmetal is used in jet engine parts.

32. Technitium (Z = 43) does not occur in nature. It is a synthetic element. It was discovered, in 1937, by Segre.

Promethium (Z = 61) does not occur in nature also.

- 33. (a) Rolled gold is an alloy of Cu (95%) and Al (5%) and is used for artificial jewellery.
  - (b) Impure zinc is called spelter.
  - (c) German silver does not contain silver. It is an alloy of Cu (56%), Zn (24%) and Ni (20%).
  - (d) Iron does not form amalgam with mercury.
  - (e) Sterling silver is an alloy of Ag (80%) and Cu (20%).
  - **Permalloy** (Fe 21%, Ni 78% + C) is strongly magnetised by electric current but loses magnetism when electric current is cut off.
  - (g) Alnico (Fe = 60%, Al = 12%, Ni = 20% and Co = 8%) is highly magnetic and is used for permanent magnets.

# -\*••- PRACTICE PROBLEMS -•••-

### Subjective Type Questions

- 1. How do the following properties vary in the transition elements?
  - (a) Atomic size
  - (b) Stability of various oxidation states
  - (c) Ionisation energy
- 2. Explain the following:
  - (a) Mercury is a liquid.
  - (b) Why CuSO<sub>4</sub> is blue while ZnSO<sub>4</sub> is white.
  - (c) Why zinc and cadmium are soft metals.
- 3. (a) Which one out of the each of following pairs is more stable?
  - (i)  $Cr^{2+}$ ,  $Cr^{3+}$  (ii)  $Fe^{3+}$ ,  $Fe^{2+}$  (iii)  $Mn^{2+}$ ,  $MnO_4^-$
  - (b) Which one of the following-tend to be an oxidising or reducing agent?
    - (i)  $Cr^{2+}$  (ii)  $Cr_2O_7^{2-}$  (iii)  $MnO_4^-$  (iv)  $Ti^{2+}$
- 4. Predict the spin only megnetic moment for:
  - (a)  $Fe^{2+}$  (b)  $Mn^{2+}$  (c)  $Cr^{6+}$  (d)  $Cu^{+}$
- 5. Answer the following:
  - Name the lightest and heaviest elements in terms of density among the transition elements.
  - (ii) Name the transition element which does not show variable oxidation states.
  - (iii) Name the member of lanthanide series which is well known to exhibit +4 oxidation state.
  - (iv) The +3 oxidation state of lanthanum (Z = 57), gadolinium (Z = 64) and lutetium (Z = 71) are especially stable.
  - (v) Why lanthanides are paramagnetic in nature?
- 6. What happens when?
  - (i) Hot and concentrated nitric acid reacts with copper.
  - (ii) Copper sulphate reacts with potassium iodide.
  - (iii) Ammonia solution is added to copper sulphate solution.
    [M.L.N.R. 1991]
  - (iv) Cupric chloride is heated with concentrated HCl and copper turnings.
  - (v) Copper is heated with concentrated H<sub>2</sub>SO<sub>4</sub>.
  - (vi) Potassium iodide is added first and then sodium thiosulphate to a solution of copper sulphate.
  - (vii) Sulphur dioxide is circulated through a solution of copper sulphate containing sodium chloride.
  - (viii) Silver chloride is treated with excess of ammonium hydroxide.
  - (ix) Gold is dissolved in aqua-regia.
  - (x) Sodium thiosulphate solution is added to silver bromide.
- 7. What happens when?
  - (i) Excess of caustic soda solution is added slowly to zinc chloride solution.
  - (ii) Excess of ammonium hydroxide solution is added to zinc chloride solution.
  - (iii) Mercuric chloride is treated with NH4OH.

- (iv) Mercurous chloride is treated with NH<sub>4</sub>OH.
- (v) Potassium iodide is added in excess to the solution of ferric sulphate.
- (vi) Potassium permanganate solution is added to ferrous sulphate solution in presence of sulphuric acid.
- (vii) Potassium nitrite reacts with cobalt chloride in presence of acetic acid.
- (viii) H<sub>2</sub>S is circulated through acidic solution of ferric chloride.
- 8. What happens when the following chemical compounds are heated?
  - (i) Silver nitrate
- (ii) Blue vitriol
- (iii) White vitriol
- (iv) Green vitriol
- (v) Hydrated zinc chloride
- (vi) Mercurous chloride
- (vii) Zinc carbonate (ix) Zinc nitrate
- (viii) Mercuric nitrate(x) Mercuric oxide
- (ix) Zinc initale
- (xi) Hydrated ferric chloride (xii) Cupric nitrate
- 9. Complete and balance the following equations:
  - (i)  $CuSO_4 + Na_2CO_3 + H_2O \longrightarrow ... + Na_2SO_4 + ...$ 
    - [I.I.T. 1992]
  - (ii)  $CuSO_4 + NH_4OH \longrightarrow ... + ...$
  - (iii) AgBr + Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  $\longrightarrow \dots + \dots$
- [L.I.T. 1993]

- (iv)  $CuSO_4 + KI \longrightarrow ...$
- (v)  $CuSO_4 + KCN \longrightarrow ...$
- (vi)  $Ag^+ + AsH_3 + \dots \rightarrow H_3AsO_3 + H^+ + \dots$
- (vii)  $Ag + CN^- + O_2 + \dots \longrightarrow OH^- + \dots$  [Roorkee 1996]
- (viii)  $HgCl_2 + SnCl_2 \longrightarrow ...$
- (ix)  $CdSO_4 + NH_4OH \longrightarrow ...$
- (x)  $HgCl_2 + SO_2 + ... \longrightarrow ...$
- (xi)  $[Fe(H_2O)_6]^{2+} + NO_3^- + H^+ \longrightarrow \dots + [Fe(H_2O)_6]^{3+} + H_2O$  $[Fe(H_2O)_6]^{2+} + \dots \longrightarrow \dots + H_2O$  [L.T. 1993]
- (xii)  $FeCl_3 + H_2S \longrightarrow ...$
- (xiii)  $MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$ (Acidic medium) [Roorkee 1996]
- (xiv)  $Fe^{2+} + NO_3^- + H^+ \longrightarrow Fe^{3+} + ... + H_2O$  [Roorkee 1996]
- (xv)  $FeCl_3 + KI \longrightarrow ...$
- (xvi)  $Ag_2S + 2CuCl_2 + 2Hg \longrightarrow ... + ... + S + 2Ag$ [Roorkee 1998]
- (xvii) Au + HCl + HNO<sub>3</sub>  $\longrightarrow$  ... + ... + H<sub>2</sub>O [Roorkee 1999]
- (xviii)  $Cu(OH)_2 + NH_4NO_3 + NH_4OH \longrightarrow ... + H_2O$

[Roorkee 1999]

- 10. How will you obtain the following?
  - (i) Cuprous chloride from copper sulphate.
  - (ii) Silver nitrate from silver.
  - (iii) Silver from silver nitrate.
  - (iv) Mercury from corrosive sublimate.
  - (v) Zinc chloride from zinc sulphate.
  - (vi) Anhydrous ferric chloride from iron.
  - (vii) Ferric chloride from ferrous sulphate.

- 11. Give the balanced equations for the:
  - (i) Reaction of argentite with KCN. Name the products in solution. [L.I.T. 1996]
  - (ii) Recovery of silver from silver coin.
  - (iii) Extraction of copper from copper pyrites by self reduction. [I.I.T. 1990]
  - (iv) Extraction of zinc from zinc blende.
  - (v) Reactions occurring in blast furnace in the extraction of iron.
- 12. Name two principal ores of each of the following metals:
  - (i) Copper (ii) Silver (iii) Zinc (iv) Mercury (v) Iron
- 13. Give the constituents of following alloys:
  - (i) Brass (ii) German silver (iii) Bronze (iv) Rolled gold
  - (v) Constantan (vi) Invar (vii) Stainless steel (viii) Gun metal

#### 14. Answer the following:

- (i) What are d-block elements?
- (ii) What is the general electronic configuration of *d*-block elements?
- (iii) Name three characteristic properties of d-block elements.
- (iv) Name the first and last element of 3d-series.
- (v) Name the two elements of 3*d*-series which show anomalous electronic configuration.
- (vi) Transition elements form alloys easily. What is the reason?
- (vii) Which ions of first transition series show highest paramagnetism?
- (viii) Why the compounds of transition elements are coloured?
- (ix) Why Fe<sup>3+</sup> compounds are more stable?
- (x) Why most of the compounds of transition elements are paramagnetic?
- (xi) What is the maximum oxidation state of manganese?
- (xii) What is the maximum oxidation state of chromium?
- 15. Write short notes on the following:
  - (i) Refining of blister copper (ii) Silver plating
  - (iii) Silvering of mirrors
- (iv) Poling process
- (v) Cupellation process
- (vi) Galvanisation
- (vii) Lithopone
- (viii) Nessler's reagent
- (ix) Passivity
- (x) Heat treatment of steel
- (xi) Corrosion of iron
- (xii) Types of iron
- 16. Explain the following giving proper reason.
  - Anhydrous ferric chloride cannot be obtained by heating hydrated ferric chloride.

[Hint: On heating, it reacts with water of crystallisation and converted into  $Fe_2O_3$  with evolution of HCl.

$$2[FeCl_3·6H_2O] \xrightarrow{Heat} Fe_2O_3 + 6HCl + 9H_2O]$$

(ii) ZnO is used as a white paint inspite of the fact that it has less covering power than white lead.

[Hint: ZnO is not blackened in atmosphere of hydrogen sulphide. It can be used both as oil and water paint. It is non-poisonous in nature.]

(iii) CuSO<sub>4</sub> is paramagnetic while ZnSO<sub>4</sub> is diamagnetic.

[Hint:  $Cu^{2+}$  ion has  $3d^9$  configuration, *i.e.*, one unpaired orbital while  $Zn^{2+}$  ion has  $3d^{10}$  configuration, *i.e.*, all orbitals doubly occupied.]

(iv) Hydrated zinc chloride cannot be dehydrated on heating?
 [Hint: On heating it reacts with water of crystallisation and forms zinc oxychloride.

$$2ZnCl_2 \cdot 2H_2O \longrightarrow Zn_2OCl_2 + 2HCl + 3H_2O$$

(v) Zinc is used in the galvanisation of iron.

[Hint: Zinc coating protects the iron from corrosion as zinc is not affected by oxygen and water.]

(vi) Poling process is used in the purification of copper.

[Hint: The oxide of copper which remains in the copper (blister) is reduced by introducing poles of green wood. The gas (hydrocarbons, CO, H<sub>2</sub>, etc.) bubbles originating from the wood act as reducing agents. The mass is stirred with these green poles vigorously.]

(vii) A solution of ferric chloride gives a brown precipitate on standing.

[Hint: Hydrolysis of ferric chloride occurs giving finally brown precipitate.

FeCl<sub>3</sub> + 
$$3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

$$2Fe(OH)_3 \longrightarrow Fe_2O_3 + 3H_2O]$$
Brown

(viii) Transition metals and their compounds act as catalysts.
 [Hint: Because of the availability of d-orbitals they can easily form intermediate products which are activated. The

sizes of transition metal atoms and ions are also favourable for transitory complex formation with the reactants.]

(ix) In moist air copper corrodes to produce a green layer on the surface. [I.I.T. 1998]

[Hint: Copper in presence of moisture oxygen and carbon dioxide of atmosphere is converted into basic carbonate which is deposited as green layer on surface.

$$2Cu + CO_2 + H_2O + O_2 \longrightarrow Cu(OH)_2CuCO_3$$

- 17. Due to lanthanide contraction which properties are expected to be similar in the same vertical columns of the second and third row transition elements besides atomic radii?
- **18.** Calculate magnetic moments of  $M^{2+}$  ions of Ti(Z=22), Cr(Z=24), Mn(Z=25) and Cu(Z=29) and arrange them in increasing order.
- 19. Explain by giving suitable reason.
  - (i) Yellow coloured aqueous solution of sodium chromate changes to orange-red when CO<sub>2</sub> under pressure is passed.

[Hint: CO<sub>2</sub> gives H<sup>+</sup> ions which are responsible for the conversion of chromate into dichromate (orange-red).

$$CO_2+H_2O \rightleftharpoons HCO_3^2+H^+$$
  
 $2CrO_4^{2^-} + 2H^+ \longrightarrow Cr_2O_7^{2^-}+H_2O]$ 

(ii) CO<sub>2</sub> is evolved when NaHCO<sub>3</sub> is added to FeCl<sub>3</sub> solution.

[Hint: FeCl<sub>3</sub> undergoes hydrolysis giving HCl which reacts with NaHCO<sub>3</sub> to form CO<sub>2</sub>.

$$\begin{aligned} & \text{FeCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Fe(OH)}_3 + 3\text{HCl} \\ & \text{NaHCO}_3 + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 ] \end{aligned}$$

(iii) Green solution of potassium manganate, K<sub>2</sub>MnO<sub>4</sub>, turns purple when CO<sub>2</sub> is circulated.

[Hint:  $CO_2$  gives  $H^+$  ions which are responsible for conversion of  $MnO_4^{2-}$  into  $MnO_4^{-}$  (purple).

$$\begin{array}{c} CO_2\text{+}H_2O \iff H^+\text{+}HCO_3^-\\ 3MnO_4^{2^-} + 4H^+ & \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O]\\ \text{Green} \end{array}$$

(iv)  $Hg^{2+}$  and  $Hg_2^{2+}$  salts are colourless.

[Hint:  $Hg^{2+}$  and  $Hg_2^{2+}$  salts have  $5d^{10}$  configuration, i.e., there is no d-d transition, hence colourless.]

(v) Cu2+ salts are paramagnetic while Cu+ salts are diamagnetic in nature.

[Hint:  $Cu^{2+}$  configuration is  $3d^{9}$ (one orbital is singly occupied)—Paramagnetic;  $Cu^{+}$  configuration is  $3d^{10}$ (all orbitals are doubly occupied)—Diamagnetic.]

#### 20. Explain:

(a) Why is K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> generally preferred to Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in volumetric analysis?

[Hint: K2Cr2O7 is not hygroscopic and can be used as primary standard.]

(b) Which divalent metal ion has maximum paramagnetic character among the first transition metals? Why?

[Hint: Mn<sup>2+</sup>. It has maximum number of unpaired electrons.]

(c) HgCl<sub>2</sub> and SnCl<sub>2</sub> cannot exist together in an aqueous solution. Why?

[Hint: SnCl2 is a strong reducing agent. It reduces HgCl2 to

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$
  
 $Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$ 

(d) Why does AgNO<sub>3</sub> produce a black stain on the skin? [Hint: In the presence of organic matter and light, AgNO3 decomposes to give a black stain of metallic silver.

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

(e) How the colour of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution does depend on pH of the solution?

[Hint: In the solution, the following equilibria exists:

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$$

In acidic medium (pH < 7), it exists as  $Cr_2O_7^{2-}$  ions and has orange colour while in basic medium (pH>7), it exists as CrO<sub>4</sub> ions and has yellow colour.]

### ■ Matching Type Questions

#### Match the following:

- [A] (i) Corrosive sublimate
- (a) Hg<sub>2</sub>Cl<sub>2</sub>
- (ii) Vermilion
- (b) Impure zinc
- (iii) Calomel
- (c) K<sub>2</sub>HgI<sub>4</sub>+KOH

- (iv) Lithopone
- (v) Zinc oxide
- (vi) White vitriol
- (vii) Spelter
- (viii) Rinmann's green
- (ix) Nessler's reagent
- (x) Pharash's serpent
- (xi) Calamine
- (xii) Cinnabar
- [B] (i) Lunar caustic
  - (ii) Blue vitriol
  - (iii) Malachite
  - (iv) Argentite

- (d) Cobalt zincate
- (e) Hg(CNS)<sub>2</sub>
- (f) An ore of mercury
- (g) An ore of zinc
- (h) HgCl<sub>2</sub>
- (i) Zinc sulphate
- (j) (BaSO<sub>4</sub>+ZnS)
- (k) Red form of HgS
- A white pigment
- (a) Basic copper acetate
- (b) Impure copper

(e) Silver nitrate

(f) An ore of silver

(g) An ore of copper

(i) Copper sulphate

(i) Silver bromide

(d) An alloy of iron

(a)  $Fe_4[Fe(CN)_6]_3$ 

(b) Impure iron

(e) Pure iron

(f) Mixed oxide

(g) An ore of iron

(h) Galvanised iron

(FeSO<sub>4</sub>·7H<sub>2</sub>O)

(h) An alloy of copper

(c)  $FeSO_4(NH_4)_2SO_4\cdot 6H_2O_1$ 

- (c) Black oxide of copper
- (d) Mixture of copper sulphide and iron sulphide
- (v) Blister copper
- (vi) Brass
- (vii) Light sensitive
- (viii) Matte
- (ix) Verdigris
- (x) Tenorite
- [C] (i) Green vitriol
  - (ii) Haematite
  - (iii) Siderite
  - (iv) Prussian blue
  - (v) Mohr's salt
  - (vi) Pig iron

  - (vii) Wrought iron
  - (viii) Steel (stainless)

  - (ix) Resistant of corrosion (i) Ferrous sulphate

  - (x) Magnetic oxide
- [D] (i) Standard electrode
  - (ii) Silvering of mirrors
  - (iii) Electric wiring

  - (iv) Steel manufacturing
  - (v) Pig iron
  - (vi) Parkes process
  - (vii) White vitriol
  - (viii) Deacon's process
- (j) FeCO<sub>3</sub> (a) Open hearth furnace
- (b) Blast furnace
- (c) ZnSO<sub>4</sub>·7H<sub>2</sub>O
- (d) Silver
- (e) Cupric chloride
- (f) Hg<sub>2</sub>Cl<sub>2</sub>
- (g) Copper metal
- (h) AgNO<sub>3</sub>

## tuswers

#### **Answers:** Subjective Type Questions

- 1. See the trends in properties.
- (a) No metallic bond formation is present.
  - (b)  $Cu^{2+}$  in  $CuSO_4$  has [Ar]  $3d^94s^0$  configuration. It can undergo d-d transition. It absorbs red region of the visible light and hence CuSO<sub>4</sub> appears blue as blue is complimentary colour of red. In  $ZnSO_4$ ,  $Zn^{2+}$  has  $3d^{10}4s^0$  configuration. It cannot undergo d-d transition, hence it appears colourless.
  - (c) Zn and Cd have no unpaired electron and thus there is no metallic bonding. Hence, they are soft in nature.
- (a) (i)  $Cr^{3+}$  (ii)  $Fe^{3+}$  (iii)  $Mn^{2+}$ 
  - (b) (i) reducing agent (ii) oxidising agent (iii) oxidising agent (iv) reducing agent.

<b>.</b>	Ion	Electronic Configuration	No. of unpaired electrons	Magnetic moment
	(a) Fe <sup>2+</sup>	[Ar] $3d^64s^0$	4	4.90 BM
	(b) $Mn^{2+}$		. 5	5.96 BM
	(c) Cr <sup>6+</sup>	[Ar] $3d^04s^0$	0	0 BM
	(d) Cu <sup>+</sup>	[Ar] $3d^{10}4s^0$	0	0 BM

- (i) Scandium (density 3.43 g cm<sup>-3</sup>) and osmium or iridium (density 22.59 and 22.61 g cm<sup>-3</sup> resp.)
  - (ii) Scandium. It shows only +3 oxidation state.
  - (iii) Cerium (Z = 58). It has configuration [Xe]  $4f^15d^16s^2$ . After losing 4 electrons, it acquires inert gas configuration.
  - (iv) This is because they have  $4f^0$ ,  $4f^7$  (half-filled) and  $4f^{14}$  (fully filled) subshell respectively.
  - (v) All the lanthanides except La<sup>3+</sup> and Lu<sup>3+</sup> contain unpaired electrons.

**6.** (i) Cu + 4HNO<sub>3</sub>(Conc.) 
$$\xrightarrow{\text{Heat}}$$
 Cu(NO<sub>3</sub>)<sub>2</sub> + 2NO<sub>2</sub> +2H<sub>2</sub>O

- (ii)  $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$
- $CuSO_4 + 4NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$ (iii) Tetrammine cupric sulphate
- $CuCl_2 + Cu \xrightarrow{HCl} Cu_2Cl_2$ (iv)
- $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$ (v)
- $2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$ (vi)  $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

$$2\text{CuSO}_4 + 4\text{KI} + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$$

$$(\text{vii})2\text{CuSO}_4 + 2\text{NaCl} + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Cu}_2\text{Cl}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$$

(viii) AgCl + 
$$2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O$$

 $AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O$  $(ix)2Au + 3HNO_3 + 11HCl \longrightarrow 2HAuCl_4 + 3NOCl + 6H_2O$ 

Chloroauric chloride

- (x)  $AgBr + 2Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> \longrightarrow Na<sub>3</sub>[Ag(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>] + NaBr$ Sodium argentothiosulphate
- 7. (i)  $ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$

$$\frac{\text{Zn}(\text{OH})_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O}}{\text{ZnCl}_2 + 4\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + 2\text{NaCl} + 2\text{H}_2\text{O}}$$

Sodium zincate  $ZnCl_2 + 2NH_4OH \longrightarrow Zn(OH)_2 + 2NH_4Cl$ 

(ii)  $Zn(OH)_2 + 2NH_4Cl + 2NH_4OH \longrightarrow [Zn(NH_3)_4]Cl_2 + 4H_2O$ Tetrammine zinc chloride

$$ZnCl_2 + 4NH_4OH \longrightarrow [Zn(NH_3)_4]Cl_2 + 4H_2O$$

- $HgCl_2 + 2NH_4OH \longrightarrow Hg(NH_2)Cl + NH_4Cl + 2H_2O$ (iii)
- $Hg_2Cl_2+2NH_4OH \longrightarrow Hg(NH_2)Cl + Hg +NH_4Cl+2H_2O$ (iv)
- $Fe_2(SO_4)_3 + 2KI \longrightarrow 2FeSO_4 + K_2SO_4 + I_2$

(vi) 
$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$[2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + [\text{O}] \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}] \times 5$$

 $2KMnO_4+8H_2SO_4+10FeSO_4 \longrightarrow 5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O_4$ 

(vii) 
$$[CoCl_2 + 2KNO_2 \longrightarrow Co(NO_2)_2 + 2KCl] \times 2$$
  
 $[Co(NO_2)_2 + 4KNO_2 \longrightarrow K_4Co(NO_2)_6] \times 2$ 

 $[KNO_2 + CH_3COOH \longrightarrow CH_3COOK + HNO_2] \times 2$ 

$$2\text{HNO}_2 \longrightarrow 2\text{NO} + \text{H}_2\text{O} + [\text{O}]$$

$$2K_4Co(NO_2)_6 + H_2O + [O] \longrightarrow 2K_3Co(NO_2)_6 + 2KOH$$

$$[KOH + CH_3COOH \longrightarrow CH_3COOK + H_2O] \times 2$$

2CoCl<sub>2</sub>+14KNO<sub>2</sub>+4CH<sub>3</sub>COOH 
$$\longrightarrow$$
 2K<sub>3</sub>Co(NO<sub>2</sub>)<sub>6</sub> + 4CH<sub>3</sub>COOK

or 
$$CoCl_2 + 7KNO_2 + 2CH_3COOH \longrightarrow K_3Co(NO_2)_6 + 2CH_3COOK + 2KCl + NO + H_2OOK$$

(viii) 
$$2\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$$

(i) On heating above its melting point, it decomposes to silver nitrite and oxygen.

$$2AgNO_3 \longrightarrow 2AgNO_2 + O_2$$

When heated at red heat, it further decomposes to metallic silver.

$$AgNO_2 \longrightarrow Ag + NO_2$$

$$2AgNO_2 \longrightarrow 2Ag + 2NO_2 + O_3$$

or 
$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

(ii) 
$$CuSO_4 \cdot 5H_2O \xrightarrow{100^{\circ}C} CuSO_4 \cdot H_2O \xrightarrow{230^{\circ}C} CuSO_4 \xrightarrow{720^{\circ}C}$$

Blue Bluish white White

$$CuO + SO_3 \longrightarrow SO_2 + \frac{1}{2}O_2$$

$$ZnSO_4 \cdot 7H_2O \xrightarrow{Above} ZnSO_4 \cdot H_2O \xrightarrow{Above} ZnSO_4 \xrightarrow{800^{\circ}C} ZnO$$
White

White 
$$ZnSO_4 \cdot H_2O \xrightarrow{70^{\circ}C} ZnSO_4 \cdot H_2O \xrightarrow{280^{\circ}C} ZnSO_4 \xrightarrow{} ZnSO_4 \xrightarrow{} ZnOO_4 \xrightarrow{} ZnSOO_5 \xrightarrow{} ZnSOO_5 \xrightarrow{$$

(iv) 
$$2\text{FeSO}_4.7\text{H}_2\text{O} \xrightarrow{300^{\circ}\text{C}} 2\text{FeSO}_4 \xrightarrow{\text{High}} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$$

(v) 
$$ZnCl_2 \cdot 2H_2O \longrightarrow Zn(OH)Cl + HCl + H_2O$$

or 
$$2ZnCl_2 \cdot 2H_2O \longrightarrow Zn_2OCl_2 + 2HCl + 3H_2O$$
  
Zinc oxychloride

(vi)  $Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$ 

(vii) 
$$ZnCO_3 \longrightarrow ZnO + CO_2$$

(viii) 
$$2Hg(NO_3)_2 \longrightarrow 2HgO + 4NO_2 + O_2$$

or 
$$2\text{Hg(NO}_3)_2 \longrightarrow 2\text{Hg} + 4\text{NO}_2 + 2\text{O}_2$$

(ix) 
$$2Zn(NO_3)_2 \longrightarrow 2ZnO + 4NO_2 + O_2$$

(x) 
$$2HgO \longrightarrow 2Hg + O_2$$

(xi) 
$$2[FeCl_3 6H_2O] \longrightarrow Fe_2O_3 + 6HCl + 9H_2O$$

(xii) 
$$2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$$

9.  $2CuSO_4 + 2Na_2CO_3 + H_2O \longrightarrow CuCO_3 \cdot Cu(OH)_2$ + 2Na<sub>2</sub>SO<sub>4</sub> + CO<sub>2</sub>

Transition Elements or *d*-block Elements and *f*-block Elements

(ii) 
$$CuSO_4 + 4NH_4OH \longrightarrow Cu(NH_3)_4SO_4 + 4H_2O$$

(iii)  $AgCl + 2Na_2S_2O_3 \longrightarrow Na_3Ag(S_2O_3)_2 + NaCl$ 

(iv)  $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$ 

(v)  $2CuSO_4 + 10KCN \longrightarrow 2K_3Cu(CN)_4 + (CN)_2 + 2K_2SO_4$ 

(vi)  $6Ag^+ + AsH_3 + 3H_2O \longrightarrow 6Ag + 6H^+ + H_3AsO_3$ 

(vii)  $4Ag + 8CN^- + O_2 + 2H_2O \longrightarrow 4OH^- + 4[Ag(CN)_2]^-$ 

(viii)  $HgCl_2 + SnCl_2 \longrightarrow Hg + SnCl_4$ 

(ix)  $CdSO_4 + 4NH_4OH \longrightarrow Cd(NH_3)_4SO_4 + 4H_2O$ 

(x)  $2HgCl_2 + SO_2 + 2H_2O \longrightarrow Hg_2Cl_2 + 2HCl + H_2SO_4$ 

(xi)  $3[Fe(H_2O)_6]^{2+} + NO_3 + 4H^+ \longrightarrow NO + 3[Fe(H_2O)_6]^{3+} + 2H_2O$ 

[Fe(H\_2O)\_6]^{2+}  $+ NO \longrightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$ 

(xii)  $2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$ 

(xiii) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ 

(xv)  $2FeCl_3 + 2KI \longrightarrow 2FeCl_2 + 2KCl + I_2$ 

(xv)  $2FeCl_3 + 2KI \longrightarrow 2FeCl_2 + 2KCl + I_2$ 

(xvi)  $Ag_2S + 2Hg + 2CuCl_2 \longrightarrow Cu_2Cl_2 + Hg_2Cl_2 + 2Ag + S$ 

(xvii)  $Au + 4HCl + HNO_3 \longrightarrow HAuCl_4 + NO + 2H_2O$ 

(xviii)  $Cu(OH)_2 + 2NH_4NO_3 + 2NH_4OH \longrightarrow Cu(NH_3)_4(NO_3)_2 + 4H_2O$ 

10. (i)  $2CuSO_4 + 2NaCl + SO_2 + 2H_2O \longrightarrow Cu_2Cl_2 + Na_2SO_4$ 

$$+ 2H2SO4$$

Cuprous chloride

(ii) Ag + 2HNO<sub>3</sub>(conc.) 
$$\longrightarrow$$
 AgNO<sub>3</sub> + NO<sub>2</sub> + H<sub>2</sub>O

(iii) 
$$2AgNO_3 + Zn \longrightarrow 2Ag + Zn(NO_3)_2$$

(iv) 
$$HgCl_2 + SnCl_2 \longrightarrow Hg + SnCl_4$$

(v) 
$$ZnSO_4 + NaHCO_3 \longrightarrow ZnCO_3 + NaHSO_4$$
  
 $ZnCO_3 + 2HCl(dil.) \longrightarrow ZnCl_2 + H_2O + CO_2$ 

(vi) 
$$2\text{Fe} + 3\text{Cl}_2 \longrightarrow 2\text{FeCl}_3$$
 (By passing chlorine over heated iron fillings.)

(vii) 
$$2\text{FeSO}_4 \xrightarrow{\text{Heated} \atop \text{strongly}} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$$

$$Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$$
  
 $Ag_*S + 4KCN \longrightarrow 2KAg(CN)_2 + K$ 

11. (i) 
$$Ag_2S + 4KCN \rightleftharpoons 2KAg(CN)_2 + K_2S$$
Pot. argentocyanide

The above reaction is reversible. To dissolve Ag<sub>2</sub>S in KCN, air is blown through solution.

$$4K_2S + 5O_2 + 2H_2O \longrightarrow 2K_2SO_4 + 4KOH + 2S$$

(ii) Coin is dissolved in nitric acid. Silver nitrate is present in the solution. HCl is added to precipitate AgCl which is fused with Na<sub>2</sub>CO<sub>3</sub> to recover Ag.

$$AgNO_3 + HCl \longrightarrow AgCl + HNO_3$$
  
 $2AgCl + Na_2CO_3 \longrightarrow Ag_2CO_3 + 2NaCl$   
 $Ag_2CO_3 \longrightarrow 2Ag + CO_2 + \frac{1}{2}O_2$ 

 $2\text{CuFeS}_2 + \text{O}_2 \xrightarrow{\text{Heat}} \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2$ (iii) Copper pyrites

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
 Roasting  
 $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$ 

$$\begin{array}{ccc} \text{FeO} + \text{SiO}_2 & \longrightarrow \text{FeSiO}_3(\text{Slag}) & \text{Smelting} \\ \text{Cu}_2\text{O} + \text{FeS} & \longrightarrow \text{Cu}_2\text{S} + \text{FeO} \\ \text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} & \longrightarrow \text{6Cu} + \text{SO}_2 & \text{Bessemerisation} \end{array}$$

(iv) 
$$2ZnS + 3O_2 \xrightarrow{900^{\circ}C} 2ZnO + 2SO_2$$

Roasting in reverberatory furnace

$$ZnO + C \longrightarrow Zn + CO$$
 Reduction

(v) Combustion zone

$$C + O_2 \longrightarrow CO_2 + 97.0 \text{ kcal}$$
  
 $CO_2 + C \xrightarrow{1500^{\circ}C} 2CO$ 

#### Reduction zone

$$3\operatorname{Fe}_{2}\operatorname{O}_{3} + \operatorname{CO} \xrightarrow{300-400^{\circ}\operatorname{C}} 2\operatorname{Fe}_{3}\operatorname{O}_{4} + \operatorname{CO}_{2}$$

$$\operatorname{Fe}_{3}\operatorname{O}_{4} + \operatorname{CO} \xrightarrow{500-600^{\circ}\operatorname{C}} 3\operatorname{FeO} + \operatorname{CO}_{2}$$

$$\operatorname{FeO} + \operatorname{CO} \xrightarrow{700^{\circ}\operatorname{C}} \operatorname{Fe} + \operatorname{CO}_{2}$$

#### Slag formation zone

$$\begin{array}{c} \text{CaCO}_3 \xrightarrow{1000^{\circ}\text{C}} \text{CaO} + \text{CO}_2 \\ \text{CaO} + \text{SiO}_2 &\longrightarrow \text{CaSiO}_3(\text{Slag}) \\ \text{P}_4\text{O}_{10} + 10\text{C} &\longrightarrow 4\text{P} + 10\text{CO} \\ \text{SiO}_2 + 2\text{C} &\longrightarrow \text{Si} + 2\text{CO} \\ \text{MnO}_2 + 2\text{C} &\longrightarrow \text{Mn} + 2\text{CO} \end{array}$$

These are partly absorbed by iron.

- 12. (i) Copper pyrites, CuFeS<sub>2</sub>;
  - (ii) Argentite Ag<sub>2</sub>S;

  - (iii) Zinc blende ZnS; (iv) Cinnabar HgS;
- Argentiferous lead Calamine ZnCO<sub>3</sub>

Copper glance; Cu2S

- Small quantities of Hg
  - occur in free condition
- (v) Haematite Fe<sub>2</sub>O<sub>3</sub>; Magnetic Fe<sub>3</sub>O<sub>4</sub>
- 13. (i) Cu and Zn (ii) Cu, Zn and Ni (iii) Cu and Sn (iv) Cu and Al (v) Cu and Ni (vi) Fe and Ni (vii) Fe, Cr and Ni (viii) Cu, Sn and Zn
- (i) The elements in which differentiating electron is accommodated in the d-subshell are called d-block elements. (ii)  $(n-1)d^{1-10}ns^2$ (iii) (a) Formation of coloured compounds (b) Formation of complex compounds (c) Paramagnetic in nature (iv) Scandium, Zinc (v) Chromium, Copper (vi) Nearly same atomic radii (vii) Fe<sup>3+</sup> and Mn<sup>2+</sup> (viii) d-d transition by absorbing part of visible light (ix)  $3d^3$  configuration, i.e., all the five orbitals are singly occupied (x) Presence of unpaired electrons (xi) +7 (xii) +6.
- 15. See text.
- 17. Lattice energies, solution energies and ionisation energies.

**18.** 
$$\text{Ti}^{2+} = \sqrt{8}$$
;  $\text{Cr}^{2+} = \sqrt{24}$ ;  $\text{Mn}^{2+} = \sqrt{35}$ ;  $\text{Cu}^{2+} = \sqrt{3}$   
 $\text{Cu}^{2+} < \text{Ti}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+}$ 

#### Answers: Matching Type Questions

- $[A] \ (i-h); \ (ii-k); \ (iii-a); \ (iv-j); \ (v-l); \ (vi-i); \ (vii-b);$ (viii-d); (ix-c); (x-e); (xi-g); (xii-f).
- [B] (i-e); (ii-i); (iii-g); (iv-f); (v-b); (vi-h); (vii-j); (viii-d); (ix-a); (x-c).
- [C] (i-i); (ii-g); (iii-j); (iv-a); (v-c); (vi-b); (vi-e); (viii—d); (ix—h); (x—f).
- [D] (i—f); (ii—h); (iii—g); (iv—a); (v—b); (vi—d); (vii—c); (viii-e).

### QUESTIONS BASED ON THE PROPERTIES

- 1. An unknown inorganic compound (A) gave the following reactions:
  - (a) The compound (A) on heating gave a residue and a gaseous mixture of NO<sub>2</sub> and oxygen.
  - (b) The compound (A) with tap water gave a turbidity which did not dissolve in conc. HNO<sub>3</sub>.
  - (c) The aqueous solution of (A) gave a white precipitate with sodium chloride solution. The precipitate dissolves in excess of ammonium hydroxide.

Identify the compound (A) and give the balanced equations. [Ans. The compound (A) is AgNO<sub>3</sub>

(a) 
$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$
  
(b)  $AgNO_3 + Cl \longrightarrow AgCl + NO_3$   
(c)  $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$   
 $AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O]$ 

2. A black coloured compound (A) on reaction with dilute H<sub>2</sub>SO<sub>4</sub> gives a gas (B) which on passing in a solution of acid (C) gives a white turbidity (D). Gas (B) when passed in an acidified solution of compound (E) gives a precipitate (F) soluble in dil. HNO<sub>3</sub>. After boiling this solution when an excess of NH<sub>4</sub>OH is added, a blue coloured compound (G) is formed. To this solution on addition of acetic acid and aqueous potassium ferrocyanide a chocolate precipitate (H) is obtained. On addition of an aqueous solution of barium chloride to an aqueous solution of (E), a white precipitate insoluble in HNO<sub>3</sub> is obtained. Identify from (A) to (H).

$$[\textbf{Hint}: \quad \text{FeS} + \text{H}_2\text{SO}_4 \longrightarrow \text{FeSO}_4 + \text{H}_2\text{S} \\ (A) \qquad \qquad (B) \\ \\ \text{H}_2\text{S} + [O] \longrightarrow \text{H}_2\text{O} + \text{S} \\ \text{From acid} \qquad (D) \\ (\text{HNO}_3) \\ \\ \text{H}_2\text{S} + \text{CuSO}_4 \longrightarrow \text{CuS} + \text{H}_2\text{SO}_4 \\ (E) \qquad \qquad (F) \\ \text{Soluble in HNO}_3 \\ \\ \text{2HNO}_3 \longrightarrow \text{H}_2\text{O} + 2\text{NO}_2 + [O] \\ \\ \text{CuS} + 2\text{HNO}_3 + [O] \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{O} + \text{S} \\ \\ \text{Cu}(\text{NO}_3)_2 + 4\text{NH}_4\text{OH} \longrightarrow \text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2 + 4\text{H}_2\text{O} \\ \\ \text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2 + 4\text{CH}_3\text{COOH} \longrightarrow \text{Cu}(\text{NO}_3)_2 + 4\text{CH}_3\text{COONH}_4 \\ \\ \text{2Cu}(\text{NO}_3)_2 + \text{K}_4\text{Fe}(\text{CN})_6 \longrightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] + 4\text{KNO}_3 \\ \\ \text{(E)} \qquad \qquad \text{CuCl}_2 + \text{BaSO}_4 \\ \\ \text{Insoluble in HNO}_3 \end{bmatrix}$$

- 3. An aqueous solution of an inorganic compound (X) gives the following reactions:
  - (a) When an aqueous solution of barium chloride is added, a precipitate insoluble in dil. HCl is obtained.
  - (b) Addition of excess of KI gives a brown precipitate which turns white on addition of excess of hypo.
  - (c) With an aqueous solution of potassium ferrocyanide a chocolate coloured precipitate is formed.

Identify (X) and give equations for the above reactions.

[Hint: The compound (X) is 
$$CuSO_4 \cdot 5H_2O$$
(a)  $CuSO_4 + BaCl_2 \longrightarrow BaSO_4 + CuCl_2$ 
Insoluble
(b)  $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$ 
White
$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$
(c)  $2CuSO_4 + K_4Fe(CN)_6 \longrightarrow Cu_2Fe(CN)_6 + 2K_2SO_4$ 

$$Chocolate ppt.$$

**4.** A certain metal (A) is boiled in dilute nitric acid to give a salt (B) and an oxide of nitrogen (C). An aqueous solution of (B) with brine solution gives a precipitate (D) which is soluble in ammonium hydroxide. On adding aqueous solution of (B) to hypo solution, a white precipitate (E) is obtained. (E) on standing turns to a black compound (F). Identify (A) to (F).

[Ans. (A) = Silver; (B) = AgNO<sub>3</sub>; (C) = NO; (D) = AgCl;

$$(E) = Ag_2S_2O_3; (F) = Ag_2S.$$
**Reactions:**  $3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO + 2H_2O$ 

$$(A) \qquad (B) \qquad (C)$$

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

$$(D)$$

$$AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O$$
Soluble
$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$$

$$(E) \text{ White ppt.}$$

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4 ]$$

$$(F) \text{ Black}$$

5. A pale blue crystalline substance (X) when heated upto 300°C gives a white solid (Y) which can restore blue colour with moisture. Solution of either (X) or (Y) forms (Z) with excess of ammonia which imparts deep blue colour to solution. Write formulae for (X), (Y) and (Z).

[Ans. 
$$(X) = \text{CuSO}_4.5\text{H}_2\text{O}; (Y) = \text{CuSO}_4; (Z) = \text{Cu}(\text{NH}_3)_4\text{SO}_4$$
]

- **6.** (i) A white amorphous powder (A) on strong heating gives a colourless non-combustible gas (B) and solid (C).
  - (ii) The gas (B) turns lime water milky and turbidity disappears with the passage of excess of gas.
  - (iii) The solution of (C) in dil. HCl gives a white precipitate with an aqueous solution of  $K_4$ Fe $(CN)_6$ .
  - (iv) The solution (A) in dilute HCl gives a white precipitate
     (D) on passing H<sub>2</sub>S in presence of excess of NH<sub>4</sub>OH.
     Identify (A) to (D) and give chemical equations for the reactions.

    [Roorkee 1993]

$$[\textbf{Hint}: ZnCO_3 \longrightarrow CO_2 + ZnO \atop (A) \qquad (B) \qquad (C) \atop (B) \qquad (C) \qquad CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \qquad \frac{CO_2}{Milky} \qquad Ca(HCO_3)_2 \atop Soluble \qquad Soluble \qquad ZnO + HCl \longrightarrow ZnCl_2 \qquad \frac{K_4Fe(CN)_6}{White \ ppt.} \qquad ZnCO_3 + HCl \longrightarrow ZnCl_2 \atop Solution \qquad ZnCl_2 + NH_4OH + H_2S \longrightarrow ZnS \qquad ] \\ White \ ppt. \qquad (D)$$

- 7. A white substance when heated in a test tube, produced a colourless, odourless gas leaving a residue, yellow when hot and white on cooling. The residue was dissolved in dil. HCl, made alkaline with ammonium chloride and ammonium hydroxide and H<sub>2</sub>S gas passed through it. A white precipitate was obtained.
  - (i) What was the original substance?
  - Write the equation for the action of heat.
  - (iii) What was the white precipitate formed with H<sub>2</sub>S? [Ans. (i)  $ZnCO_3$ ; (ii)  $ZnCO_3 \longrightarrow ZnO + CO_2$ ; (iii) ZnS]
- **8.** (i) An aqueous solution of a white coloured compound (A) on reaction with HCl gives a white precipitate of compound (B).
  - (ii) (B) becomes soluble in chlorine water with formation of
  - (iii) (C) reacts with KI to give a precipitate which becomes soluble in excess of it forming a compound (D). The compound (D) is used for detecting ammonium salts.
  - (iv) (B) and (C) both on treatment with SnCl<sub>2</sub> gives a grey precipitate of (E).
  - (v) When conc. H<sub>2</sub>SO<sub>4</sub> is added slowly into a mixture of cold solution of (A) and FeSO<sub>4</sub>, a brown ring compound (F) is formed.

Identify (A) to (F) and give chemical equations for the reactions at steps (i) to (v). [Roorkee 1997] [Ans.  $(A) = Hg_2(NO_3)_2$ ;  $(B) = Hg_2Cl_2$ ;  $(C) = HgCl_2$ ;  $(D) = K_2HgL_4$ ;  $(E) = \text{Hg}; (F) = \text{FeSO}_4 \cdot \text{NO}.$ 

**Reactions :** (i)  $Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 + 2HNO_3$ 

(ii)  $Hg_2Cl_2 + 2Cl(Chlorine water) \longrightarrow 2HgCl_2$ 

(iii) 
$$HgCl_2 + 4KI \longrightarrow K_2HgI_4 + 2KCl$$

(iv) 
$$\begin{array}{ccc} \text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 & \longrightarrow & 2\text{Hg} + \text{SnCl}_4 \\ \text{(B)} & \text{(E)} & \text{(E)} \\ \text{HgCl}_2 + \text{SnCl}_2 & \longrightarrow & \text{Hg} + \text{SnCl}_4 \\ \text{(C)} & \text{(E)} & \text{(E)} \end{array}$$

(v) 
$$Hg_2(NO_3)_2 + H_2SO_4 \longrightarrow Hg_2SO_4 + 2HNO_3$$
  
 $2HNO_3 \longrightarrow H_2O + 2NO + 3[O]$   
 $2FeSO_4 + [O] + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O$   
 $FeSO_4 + NO \longrightarrow FeSO_4 NO \quad (Brown ring)]$ 

- 9. (i) A blue coloured compound (A) on heating gives two products, (B) and (C).
  - A metal (D) is deposited on passing hydrogen through heated (B).
  - (iii) The solution of (B) in HCl on treatment with K<sub>4</sub>Fe(CN)<sub>6</sub> gives a chocolate brown coloured precipitate of compound (E).
  - (iv) (C) turns lime water milky which disappears on continuous passage of (C) forming a compound (F).

Identify (A) to (F) and give chemical equations for the reactions at steps (i) to (iv). [Roorkee 1997] [Ans. (A) =  $CuCO_3$ ; (B) = CuO; (C) =  $CO_2$ ; (D) = Cu;

 $(E) = \text{Cu}_2\text{Fe}(\text{CN})_6; \quad (F) = \text{Ca}(\text{HCO}_3)_2.$ Reactions: (i)

 $CuCO_3 \longrightarrow CuO + CO_2$ (A) (B)

(ii) 
$$CuO + H_2 \longrightarrow Cu + H_2O$$

$$(D)$$

(iii) 
$$\text{CuO} + 2\text{HCl} \longrightarrow \text{CuCl}_2 + \text{H}_2\text{O}$$
  
 $2\text{CuCl}_2 + \text{K}_4\text{Fe}(\text{CN})_6 \longrightarrow \text{Cu}_2\text{Fe}(\text{CN})_6 + 4\text{KCl}$   
(E)

(iv) 
$$\begin{array}{ccc} CO_2 + Ca(OH)_2 & \longrightarrow & CaCO_3 + H_2O \\ & & CaCO_3 + CO_2 + H_2O & \longrightarrow & Ca(HCO_3)_2 \end{array} ]$$

- **10.** (i) A black mineral (A) on heating in presence of air gives a gas (B).
  - The mineral (A) on reaction with dilute H<sub>2</sub>SO<sub>4</sub> gives a gas (C) and the solution of a compound (D).
  - (iii) On passing gas (C) into an aqueous solution of (B), a white turbidity is obtained.
  - (iv) The aqueous solution of compound (D) on reaction with potassium ferricyanide gives a blue compound (E).

Identify (A) to (E) and give chemical equation for reactions at steps (i) to (iv),

[**Hint**: (A) = FeS;  $(B) = \text{SO}_2$ ;  $(C) = \text{H}_2\text{S}$ ;  $(D) = \text{FeSO}_4$ ;  $(E) = K^{\dagger}Fe^{II}[Fe^{III}(CN)_{6}]$ 

(i) 
$$2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2$$
(A) (B)

(ii) 
$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$
(D) (C)

(iii) 
$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$
  
(C) (B) Turbidity

$$\begin{array}{ccc} \text{(iv)} & & \text{FeSO}_4 + \text{ } \text{K}_3\text{Fe}(\text{CN})_6 \longrightarrow \text{KFe}[\text{Fe}(\text{CN})_6] + \text{ } \text{K}_2\text{SO}_4] \\ & & \text{(\it{E}) Blue} \end{array}$$

11. A certain inorganic compound (A) on heating loses its water of crystallization. On further heating a blackish brown powder (B) and two oxides of sulphur, (C) and (D) are obtained. The powder (B) on boiling with hydrochloric acid gives a yellow solution (E). When  $H_2S$  is passed in (E) a white turbidity (F) and a apple green colour (G) are obtained. The solution (E) on treatment with thiocyanate ions gives a blood red coloured compound (H). Identify from (A) to (H).

[Ans. (A) =  $FeSO_4$ ·7H<sub>2</sub>O; (B) =  $Fe_2O_3$ ; (C) =  $SO_2$ ; (D) =  $SO_3$ ;  $(E) = \operatorname{FeCl}_3$ ; (F) = S;  $(G) = \operatorname{FeCl}_2$ ;  $(H) = \operatorname{Fe(SCN)}_3$ .

Reaction:

FeSO<sub>4</sub>7H<sub>2</sub>O 
$$\xrightarrow{\text{Heat}}$$
 FeSO<sub>4</sub>  $\xrightarrow{\text{Heat}}$  Fe<sub>2</sub>O<sub>3</sub> + SO<sub>2</sub> + SO<sub>3</sub>
(A) Fe<sub>2</sub>O<sub>3</sub> + 6HCl  $\longrightarrow$  2FeCl<sub>3</sub> + 3H<sub>2</sub>O

2FeCl<sub>3</sub> + H<sub>2</sub>S  $\longrightarrow$  2FeCl<sub>2</sub> + 2HCl + S
(G) (F)

FeCl<sub>3</sub> + 3SCN<sup>-</sup>  $\longrightarrow$  Fe(SCN)<sub>3</sub> + 3Cl<sup>-</sup>]

- **12.** Compound (A) is a light green solid. It gives following tests:
  - (a) It dissolves in dilute H<sub>2</sub>SO<sub>4</sub>. No gas is evolved.
  - (b) A drop of KMnO<sub>4</sub> is added to the above solution. The pink colour is decolourised.
  - (c) Compound (A) is heated strongly. Gases (B) and (C) with pungent smell come out and a brown residue (D) is left.
  - (d) The gaseous mixture is passed into a dichromate solution, it turns green.

- (e) The green solution from reaction 'd' gives a white precipitate (E) with a solution of barium nitrate.
- (f) The residue (D) from reaction 'c' on heating with charcoal in a reducing flame, gave a magnetic substance. Name the compounds (A), (B), (C), (D) and (E).

[Ans. (A) =  $FeSO_4 \cdot 7H_2O$ ; (B) =  $SO_2$ ; (C) =  $SO_3$ ; (D) =  $Fe_2O_3$ ; (E) =  $BaSO_4$ 

(a) (A) dissolves in dilute H<sub>2</sub>SO<sub>4</sub>. No gas is evolved.

(b)  $10\text{FeSO}_4 + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 \longrightarrow 5\text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{C}_4 + 8\text{H}_2\text{$ 

(c)  $2\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_2 + 2\text{SO}_3 + 14\text{H}_2\text{O}$ (A) (B) (C)

(d)  $SO_2$  reduces acidified  $K_2Cr_2O_7$ .  $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O_4$ .

- (e)  $SO_4^{2-} + Ba(NO_3)_2 \longrightarrow BaSO_4 + 2NO_3^{-}$
- (f)  $Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$
- 13. Compound (A),
  - (i) On strong heating gives two oxides of sulphur.
  - (ii) On adding aqueous NaOH solution to its aqueous solution, a dirty green precipitate is obtained which starts turning brown on exposure to air.

Identify (A) and give chemical equations. [Roorkee 1993] [Hint:  $(A) = FeSO_4$ 

$$2FeSO_{4} \xrightarrow{Heat} Fe_{2}O_{3} + SO_{2} + SO_{3}$$

$$FeSO_{4} + 2NaOH \longrightarrow Fe(OH)_{2} + Na_{2}SO_{4}$$

$$Fe(OH)_{2} \xrightarrow{[O]} Fe(OH)_{3}]$$

- **14.** A light bluish green crystalline compound corresponds to the following tests:
  - (i) Its aqueous solution gives a brown precipitate or colouration with alkaline K<sub>2</sub>[HgI<sub>4</sub>].
  - (ii) Its aqueous solution gives a blue colour with K<sub>3</sub>Fe(CN)<sub>6</sub> solution.
  - (iii) Its solution in HCl gives a white precipitate with BaCl<sub>2</sub> solution.

Identify the ions present and suggest the formula of the compound. [I.I.T. 1992]

[Ans. The ions present are NH<sub>4</sub>, Fe<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. The formula of the compound is (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·FeSO<sub>4</sub>·6H<sub>2</sub>O]

- **15.** (i) The yellow coloured precipitate of compound (A) is formed on passing H<sub>2</sub>S through a neutral solution of a salt (B).
  - (ii) (A) is soluble in hot dilute HNO<sub>3</sub>, but insoluble in yellow ammonium sulphide.
  - (iii) The solution of (B) on treatment with small quantity of NH<sub>3</sub> gives white precipitate which becomes soluble in excess of it forming a compound (C).
  - (iv) The solution of (B) gives white precipitate with small concentration of KCN which becomes soluble in excess of this reagent forming a compound (D).
  - (v) The solution of (D) on treatment with  $H_2S$  gives (A).
  - (vi) The solution of (B) in dilute HCl on treatment with a solution of BaCl<sub>2</sub> gives white precipitate of compound (E) which is insoluble in conc. HNO<sub>3</sub>.

Identify (A) to (E) and give chemical equations for the reactions at steps (i) and (iii) to (vi). [Roorkee 1998] [Hint: (B) is CdSO<sub>4</sub> which gives a yellow compound by passing H<sub>2</sub>S through its solution. It gives a white ppt. with BaCl<sub>2</sub> soln. The ppt. is insoluble in conc. HNO<sub>3</sub>. It suggests that SO<sub>4</sub><sup>2-</sup> ion is present in the salt.

(i) 
$$CdSO_4 + H_2S \longrightarrow CdS + H_2SO_4$$
  
(ii)  $CdSO_4 + BaCl_2 \longrightarrow BaSO_4 + CdCl_2$ 

(a) 
$$CdSO_4 + BaCl_2 \longrightarrow BaSO_4 + CdCl_2$$
  
(B) (E) Insoluble in water  $CdS + 2HNO_3 \longrightarrow Cd(NO_3)_2 + H_2S$ 

$$\begin{array}{c} \text{Soluble} \\ \text{CdS} + (\text{NH}_4)_2 S_x \longrightarrow \text{Insoluble} \\ \text{Yellow ammonium} \\ \text{Sulphide} \end{array}$$

(iii) 
$$CdSO_4 + 2NH_4OH \longrightarrow Cd(OH)_2 + (NH_4)_2SO_4$$
  
 $Cd(OH)_2 + 4NH_4OH \longrightarrow Cd(NH_3)_4(OH)_2 + 4H_2O$   
(C) Soluble

(iv) 
$$CdSO_4 + 2KCN \longrightarrow Cd(CN)_2 + K_2SO_4$$
White ppt.
$$Cd(CN)_2 + 2KCN \longrightarrow K_2Cd(CN)_4$$
(D) Soluble

(v) 
$$K_2Cd(CN)_4$$
 +  $H_2S \longrightarrow CdS + 2KCN + 2HCN$ 

- **16.** (i) An aqueous solution of a compound (A) is acidic towards litmus and (A) is sublimed at about 300°C.
  - (ii) (A) on treatment with an excess of NH<sub>4</sub>CNS gives a red coloured compound (B) and on treatment with a solution of K<sub>4</sub>Fe(CN)<sub>6</sub> gives a blue coloured compound (C).
  - (iii) (A) on heating with excess of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in presence of conc. H<sub>2</sub>SO<sub>4</sub> gives deep red vapours of (D).
  - (iv) On passing vapours of (D) into a solution of NaOH and then adding the solution of acetic acid and lead acetate, a yellow precipitate of compound (E) is obtained.

Identify (A) to (E) and give chemical equations for the reactions at steps (ii) to (iv). [Roorkee 1998] [Hint: (A) is FeCl<sub>3</sub>. It gives red colour of Fe(CNS)<sub>3</sub> with NH<sub>4</sub>CNS

Hint: (A) is FeCl<sub>3</sub>. It gives red colour of Fe(CNS)<sub>3</sub> with NH<sub>4</sub>CN and chromyl chloride test for Cl<sup>-</sup> ion. The reactions are:

(i) 
$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$
(A) (Acidic)

(A) sublimes at 300°C

(ii) FeCl<sub>3</sub> + 3NH<sub>4</sub>CNS 
$$\longrightarrow$$
 Fe(CNS)<sub>3</sub> + 3NH<sub>4</sub>Cl  
(B) Red  
4FeCl<sub>3</sub> + 3K<sub>4</sub>Fe(CN)<sub>6</sub>  $\longrightarrow$  Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub> + 12KCl  
(C) Blue

(iii)  $4\text{FeCl}_3 + 9\text{H}_2\text{SO}_4 + 3\text{K}_2\text{Cr}_2\text{O}_7 \longrightarrow 6\text{CrO}_2\text{Cl}_2 + 2\text{Fe}_2(\text{SO}_4)_3 + 3\text{K}_2\text{SO}_4 + 9\text{H}_2\text{O}_4$ (D) Red vapours

(iv) 
$$CrO_2Cl_2 + 4NaOH \longrightarrow 4Na_2CrO_4 + 2NaCI + 2H_2O$$
  
 $Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4 + 2CH_3COONa]$   
(E) Yellow ppt.

- 17. Pyrolusite on heating with KOH in the presence of air gives a dark green compound (A). The solution of (A) on treatment with  $H_2SO_4$  gives a purple coloured compound (B), which gives following reactions.
  - (i) KI on reaction with alkaline solution of (B) changes into a compound (C).

- (ii) The colour of the compound (B) disappears on treatment with the acidic solution of FeSO<sub>4</sub>.
- (iii) With conc. H<sub>2</sub>SO<sub>4</sub> compound (B) gives (D) which can decompose to yield (E) and oxygen.

Identify (A) to (E) and write balanced chemical equations for the formation of (A) and (B) and for steps (i) to (iii).

[Roorkee 1999]

[Hint: 
$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$
(Air) (A) Dark green
$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2SO_4 + 2H_2O$$
(B) Purple
(i)  $2KMnO_4 + H_2O + KI \longrightarrow KIO_3 + 2MnO_2 + 2KOH$ 
(ii)  $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4$ 

$$(11) 2KVM1O_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2VM1SO_4 + 5Fe_2(SO_4)_3 + 8H_2O_4$$

(iii) 
$$2\text{KMnO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Mn}_2\text{O}_7 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}_4$$

$$(D)$$

$$2\text{Mn}_2\text{O}_7 \longrightarrow 4\text{MnO}_2 + 3\text{O}_2$$

18. An aqueous blue coloured solution of a transition metal sulphate reacts with H<sub>2</sub>S in acidic medium to give a black precipitate (A) which is insoluble in warm aqueous solution of KOH. The blue solution on treatment with KI in weakly acidic medium turns yellow and produces a white precipitate (B). Identify the transition metal ion. Write the chemical reactions involved in the formation of (A) and (B).

[L.I.T. 2000]

[Hint: The transition metal ion is Cu<sup>2+</sup>.

$$\begin{array}{c} \text{CuSO}_4 + \text{H}_2\text{S} \longrightarrow \text{CuS} + \text{H}_2\text{SO}_4 \\ \text{Blue coloured} & (A) \\ \text{solution} & \text{Black ppt.} \\ \text{CuSO}_4 + 2\text{KI} \longrightarrow \text{CuI}_2 + \text{K}_2\text{SO}_4 \\ 2\text{CuI}_2 \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2 \text{]} \\ & (B) \\ \text{White not} \end{array}$$

- 19. (i) An ore (A) on roasting with sodium carbonate and lime in the presence of air gives two compounds, (B) and (C).
  - (ii) The solution of (B) in conc. HCl on treatment with potassium ferrocyanide gives a blue colour or precipitate of compound (D).
  - (iii) The aqueous solution of (C) on treatment with conc.  $H_2SO_4$  gives a yellow coloured compound (E).
  - (iv) Compound (E) when treated with KCl gives an orangered compound (F) which is used as an oxidising reagent.
  - (v) The solution of (F) on treatment with oxalic acid and then with an excess of potassium oxalate gives blue crystals of compound (G).

Identify (A) to (G) and give balanced chemical equations for reactions at steps (i) to (v). [Roorkee 2000] [Hint: The ore is chromite,  $FeOCr_2O_3$ .

(i)  $^{4}\text{FeO Cr}_{2}\text{O}_{3} + ^{8}\text{Na}_{2}\text{CO}_{3} + ^{7}\text{O}_{2} \xrightarrow{\text{Lime}} ^{\text{Lime}} ^{2}\text{Fe}_{2}\text{O}_{3} + ^{8}\text{Na}_{2}\text{CrO}_{4}$   $^{(B)} \cdot ^{(C)} \cdot ^{(C)} + ^{8}\text{CO}_{2}$ 

(ii) 
$$Fe_2O_3 + 6HC1 \longrightarrow 2FeCl_3 + 3H_2O$$

$$\begin{array}{c} \text{4FeCl}_3 + 3\text{K}_4\text{Fe}(\text{CN})_6 \longrightarrow & \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl} \\ \text{Prussian blue} \end{array}$$

(iii) 
$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

$$(C)$$
Yellow coloured

(iv) 
$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

(F)

Orange-red

(v) 
$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2C_2O_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 6CO_2 + 7H_2O$$

$$Cr_2(SO_4)_3 + 6K_2C_2O_4 \longrightarrow 2K_3[Cr_2(C_2O_4)_3] + 3K_2SO_4]$$
(G)
Blue crystals

**20.** Complete the following by identifying (A) to (F).

(i) 
$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow{100^{\circ}\text{C}} (A) \xrightarrow{230^{\circ}\text{C}} (B) \xrightarrow{800^{\circ}\text{C}} (C) + (D)$$

(ii) AgNO<sub>3</sub> 
$$\xrightarrow{\text{Red hot}}$$
 (E) + (F) + O<sub>2</sub> [Roorkee 2000]

[Hint: (i) (A) CuSO<sub>4</sub>·H<sub>2</sub>O; (B) CuSO<sub>4</sub>; (C) CuO; (D) SO<sub>3</sub> (ii) (E) Ag; (F) NO<sub>2</sub>

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

- 21. (i) A powdered substance (A) on treatment with fusion mixture gives a green coloured compound (B).
  - (ii) The solution of (B) in boiling water on acidification with dilute  $H_2SO_4$  gives a pink coloured compound (C).
  - (iii) The aqueous solution of (A) on treatment with NaOH and Br<sub>2</sub>-water gives a compound (D).
  - (iv) A solution of (D) in conc. HNO<sub>3</sub> on treatment with lead peroxide at boiling temperature produced a compound (E) which was of the same colour as that of (C).
  - (v) A solution of (A) in dilute HCl on treatment with a solution of barium chloride gave a white precipitate of compound (F) which was insoluble in conc. HNO<sub>3</sub> and conc. HCl.

Identify (A) to (F) and give balanced chemical equations for the reactions at steps (i) to (v). [Roorkee 2001] [Hint: (A) is MnSO<sub>4</sub>.

(i) 
$$MnSO_4 + Na_2CO_3 + 2KNO_3 \longrightarrow Na_2MnO_4 + 2KNO_2$$
(A) (B) Green coloured

$$+ Na_2SO_4 + 2CO_2$$
 (ii)  $3Na_2MnO_4 + 2H_2SO_4 \rightarrow 2NaMnO_4 + MnO_2 + 2Na_2SO_4 + 2H_2O$ 

and conc. HCl)

(ii)  $518a_2 \times 1100_4 + 211_2 \times 100_4 + 211_2$ 

(iii) MnSO<sub>4</sub> + 4NaOH + Br<sub>2</sub> 
$$\rightarrow$$
 MnO<sub>2</sub> + Na<sub>2</sub>SO<sub>4</sub> + 2NaBr + 2H<sub>2</sub>O (D)

(iv) 
$$2MnO_2 + 10HNO_3 + 5PbO_2 \longrightarrow 2HMnO_4 + 5Pb(NO_3)_2$$
(E)
Pink solution

(v) 
$$MnSO_4 + BaCl_2 \longrightarrow BaSO_4 + MnCl_2$$

(Insoluble in conc. HNO<sub>3</sub>

[Hint:  $K_2Cr_2O_7 + 7H_2SO_4 + 6KI -$ 

[Hint:  $Hg_2Cl_2 + 2NH_4OH \longrightarrow$ 

[Hint: Terbium is a lanthanide.]

(a) HgNH2Cl

(c) Hg<sub>2</sub>O

Ans. (a)

(a) Curium

Ans. (d)

This is:

(a) Zn

(c) Cu

Ans. (c)

[Hint: Brass

(a) Ti<sup>3+</sup>, Cu<sup>2+</sup>

(c) Co<sup>2+</sup>. Fe<sup>3+</sup>

**Bronze** 

(c) Uranium

8. Calomel (Hg<sub>2</sub>Cl<sub>2</sub>) on reaction with NH<sub>4</sub>OH gives:

Which of the following is not an actinide?

10. Brass, bronze and german silver have one metal in common.

Cu 60-80%,

Cu 75-90%,

# ILLUSTRATIONS OF OBJECTIVE QUESTIONS



[A.I.E.E.E. 2005]

[D.P.M.T. 2005]

 $4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$ 

(b) NH<sub>2</sub>—Hg—Hg—Cl

Hg + NH<sub>4</sub>Cl + 2H<sub>2</sub>Ol

Zn 40-20%

Sn 25-10%

Zn 24%,

(b)  $Sc^{3+}$ ,  $Zn^{2+}$ 

(d)  $Ni^{2+}$ ,  $V^{3+}$ 

(b) Californium

(d) Terbium

(b) Fe

(d) A1

(d) HgO

- 1. Among d-block elements, the most abundant element belongs to the:
  - (a) first transition series
- (b) second transition series
- (c) third transition series
- (d) fourth transition series

Ans. (a)

[Hint: Iron is the most abundant d-block metal which belongs to first transition series.]

- The 3d metal ions are generally paramagnetic in nature because:
  - (a) they form coloured salts
  - (b) they have one or more unpaired d electrons
  - (c) they have one or more paired s electrons
  - (d) they are reducing agents

Ans. (b)

[Hint: Paramagnetic nature is due to unpaired d electrons.]

- 3. The number of moles of acidified KMnO<sub>4</sub> required to convert one mole of sulphite ion into sulphate ion is:
  - (a) 2/5
- (b) 3/5
- (c) 4/5

Ans. (a)

[Hint: 
$$2MnO_4^- + 6H^+ + 5SO_3^{2-} \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O_2$$
  
 $2 \text{ moles}$  5 moles  
5 moles of  $SO_3^{2-} \equiv 2 \text{ moles}$  of  $MnO_4^-$ 

1 mole of  $SO_3^{2-} \equiv 2/5$  moles of  $MnO_4^{-}$ 

 $\equiv 2/5$  moles of KMnO<sub>4</sub>]

Which of the following ores contains both Cu and Fe?

[LLT. 2005]

- (a) Cuprite
- (b) Azurite
- (c) Chalcopyrite
- (d) Malachite

Ans. (c)

[Hint: Chalcopyrite—CuFeS<sub>2</sub>]

- The correct order of ionic radii of Ce, La, Pm and Yb in +3 oxidation state is:

  - $\begin{array}{ll} \hbox{(a)} \;\; La^{3+} < Pm^{3+} < Ce^{3+} < Yb^{3+} \\ \hbox{(b)} \;\; La^{3+} < Ce^{3+} < Pm^{3+} < Yb^{3+} \end{array}$
  - (c)  $Yb^{3+} < Ce^{3+} < Pm^{3+} < La^{3+}$
  - (d)  $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$

[Hint: Lanthanide contraction decreases atomic sizes from La<sup>3+</sup> to Lu<sup>3+</sup>. Hence, the correct order will be (d) for the given

- Heating mixture of Cu<sub>2</sub>O and Cu<sub>2</sub>S will give : [A.LE.E.E. 2005]
  - (a)  $Cu + SO_2$
- (b)  $Cu + SO_3$
- (c) CuO + CuS
- (d) Cu<sub>2</sub>SO<sub>3</sub>

Ans. (a)

[Hint:  $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$ ]

- 7. The oxidation state of chromium in the final product formed by the reaction between KI and acidified K2Cr2O7 solution [A.I.E.E.E. 2005] is:
  - (a) + 4

(b) + 6

(c) + 2

(d) + 3

Ans. (d)

[Hint:  $Sc^{3+}$  has  $3d^{0}$  configuration while  $Zn^{2+}$  has  $3d^{10}$  configuration. Hence, these ions are colourless.]

German silver Cu 56%,

Common metal is copper.]

11. Which of the following pairs of ions is colourless?

- 12. The lanthanide contraction relates to :
  - (a) atomic radii
- (b) atomic as well as  $M^{3+}$  radii

[E.A.M.C.E.T. (Engg.) 2004]

- (c) valence electrons
- (d) oxidation states

Ans. (b)

- 13. For successive members of the first row transition elements are listed below with their atomic numbers. Which one of them is expected to have the highest third ionisation enthalpy? [C.B.S.E. 2005]
  - (a) Vanadium (Z = 23)
- (b) Manganese (Z = 25)
- (c) Chromium (Z=24)
- (d) Iron (Z = 26)

Ans. (b)

[**Hint**: 
$$M^{2+} - e \xrightarrow{\text{3rd}} M^{3+}$$

 $Mn^{2+}$  has the most stable configuration, i.e.,  $3d^5$  (all the five d-orbitals are singly occupied). Hence, to remove electron from Mn<sup>2+</sup> ion requires more energy, *i.e.*, the third ionisation enthalpy of manganese is highest.]

- 14. Green vitriol is formed by:
  - (a)  $FeS_2 + CO$
- (b)  $FeS_2 + H_2O + CO_2$
- (c)  $FeS_2 + H_2O + O_2$
- (d)  $FeS_2 + CO + CO_2$

Ans. (c)

[Hint:  $2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$ ]

- 15. Stainless steel does not rust because:
  - (a) nickel present in it does not rust
  - (b) chromium and nickel combine with iron
  - (c) chromium forms an oxide layer and protects iron from rusting
  - (d) iron forms a hard chemical compound with chromium present in it

Ans. (c)

- 16. Which of the following forms with an excess of CN, a complex having coordination number two? [A.I.I.M.S. 2004]
  - (a) Cu<sup>2+</sup>

(b) Ag<sup>+</sup>

(c) Ni<sup>2+</sup>

(d) Fe<sup>2</sup>

Ans. (b)

[Hint:  $AgCN + CN^{-} \longrightarrow [Ag(CN)_{2}]^{-}$ ]

- 17. Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them?
  - (a)  $(n-1)d^8ns^2$
- (b)  $(n-1)d^5ns^1$
- (c)  $(n-1)d^3ns^2$
- (d)  $(n-1)d^5ns^2$

Ans. (d)

- **18.** The compound used in enrichment of uranium for nuclear power plant is: [A.I.I.M.S. 2006]
  - (a)  $U_3O_8$
- (b) UF<sub>6</sub>
- (c)  $UO_2(NO_3)_2$
- (d) UCl

Ans. (b)

- 19. Lanthanide contraction is caused due to : [A.I.E.E.E. 2006]
  - (a) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge
  - (b) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge

- (c) the same effective nuclear charge from Ce to Lu.
- (d) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge

Ans. (d

**20.** The spin only magnetic moment [in units of Bohr magneton] of Ni<sup>2+</sup> in aqueous solution would be (At. No. 28):

[A.I.E.E.E. 2006]

(a) 2.84

(b) 4.90

(c) 0

(d) 1.73

Ans. (a)

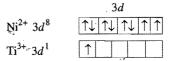
[Hint: Ni<sup>2+</sup> has  $3d^8$  configuration, *i.e.*, 2 unpaired electrons are present. Thus, magnetic moment  $= \sqrt{n(n+2)} = \sqrt{2 \times 4}$ =  $\sqrt{8} = 2.84$  B.M.]

- 21. In which of the following pairs are both the ions coloured in aqueous solution? [C.B.S.E. 2006]
  - (a)  $Sc^{3+}$ ,  $Co^{2+}$
- (b) Ni<sup>2+</sup>, Cu<sup>+</sup>
- (c)  $Ni^{2+}$ ,  $Ti^{3+}$
- (d)  $Se^{3+}$ ,  $Ti^{3+}$

[At. Nos. Sc = 21, Ti = 22, Ni = 28 and Cu = 29]

Ans. (c

[Hint: Unpaired electrons are present in  $\mathrm{Ni}^{2+}$  and  $\mathrm{Ti}^{3+}$ 



- 22. Arrange the following ions in their magnetic moment:
  - (i)  $V^{4+}$  (ii)  $Mn^{4+}$  (iii)  $Fe^{3+}$  (iv)  $Ni^{2+}$

[At. Nos. V = 23, Mn = 25, Fe = 26, Ni = 28]

- (a) (ii) > (iii) > (i) > (iv)
- (b) (iii) > (iv) > (ii) > (i)
- (c) (iii) > (ii) > (iv) > (i)
- (d) (i) < (iv) < (iii) < (ii)

Ans. (c)

[**Hint**:  $V^{4+}$ [Ar]3 $d^{1}$ , Mn<sup>4+</sup>[Ar]3 $d^{3}$ , Fe<sup>3+</sup>[Ar]3 $d^{5}$ , Ni<sup>2+</sup>[Ar]3 $d^{8}$ ]



	ODSCOTTVC GOC		
Set :	I: This set contains questions with one answer.		
	Among d-block elements, the most abundant element	11.	Among the following outermost configurations of transition
1.	belongs to:	11.	metals, which shows the highest oxidation state:
	(a) first transition series		[C.B.S.E. (P.M.T.) 2009]
	(b) second transition series		(a) $3d^3, 4s^2$
	(c) third transition series		(c) $3d^5, 4s^2$
	(d) fourth transition series	10	
2.	Which of the following is not the characteristic of transition	12.	In the first transition series, the highest oxidation state is
	metals?		exhibited by:
	(a) They are all metals		(a) Mn
	(b) They show variable oxidation states which always differ	12	_ (-)
	by two units	15.	Which of the following ions is coloured in solution?
	(c) They are paramagnetic		(a) $Zn^{2+}$ $\Box$ (b) $Ti^{4+}$ $\Box$
	(d) They easily form complexes		(c) $Cu^+$ $\Box$ (d) $V^{3+}$ $\Box$
3.	The correct order of ionisation energy is:	14.	
٠.	(a) $Cu > Ag > Au$ $\Box$ (b) $Cu > Au > Ag$ $\Box$		ion of [CoCl <sub>4</sub> ] <sup>2-</sup> ?
	(c) $Au > Cu > Ag$		(a) 5
4.	The first transition element is:		(c) 3
	(a) scandium		[Hint : $Co^{2+}$ E.C. = 2, 8, 8 + 7 $\boxed{\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow\uparrow\uparrow}$ ]
	(c) nickel		3d
5.	The general electronic configuration of transition elements	15.	Which of the following has the maximum number of unpaired
٠.	is:		d electrons?
	(a) $(n-1)d^{1-5}$		(a) $Zn$ $\Box$ (b) $Fe^{2+}$ $\Box$
	(a) $(n-1)d^{1-5}$		(c) $Ni^{3+}$ $\square$ (d) $Cu^{+}$ $\square$
6.	The property, which is not characteristic of transition metals,	16.	Colour in transition metal compounds is attributed to:
0.	is: [V.I.T.E.E.E. 2008]		(a) small size of metal ions
	(a) variable oxidation states		(b) absorption of light in UV region
•	(b) tendency to form complexes		(c) moderate ionisation energy
	(c) formation of coloured compounds		(d) incomplete $(n-1)$ $d$ subshell
	(d) natural radioactivity	17.	
7.	in a contract of the contract		(a) $f$ -block element $\Box$ (b) $d$ -block element $\Box$
	above the element with atomic number 43 in the same		(c) $p$ -block element $\square$ (d) $s$ -block element $\square$
	periodic group is:	18.	
	(a) $1s^2, 2s^22p^6, 3s^23p^63d^5, 4s^2$		(a) $[Ar]3d^9, 4s^2$
			(c) $[Ar]3d^8, 4s^2$
	(b) $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^5$	10	Which metal has the highest melting point?
	(c) $1s^2, 2s^22p^6, 3s^23p^63d^6, 4s^1$	12.	(a) Platinum
	(d) $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^14p^6$		(c) Tungsten
8.	Chromium has the electronic configuration:	20.	Transition metals show paramagnetism: [B.H.U. 2005]
	(a) $3s^23p^63d^4$ , $4s^2$	20.	(a) due to characteristic configuration
	(c) $3s^23p^63d^6$ $\square$ (d) none of these $\square$		(b) high lattice energy
9.	The number of d electrons in Fe <sup>2+</sup> (at. no. of iron = 26) is not		(c) due to variable oxidation states
7,	•		(d) due to unpaired electrons
	equal to that of:	21	Zr and Hf have almost equal atomic and ionic radii because:
	(a) $p$ electrons in neon (at. no. = 10)	21.	(a) of diagonal relationship
	(-),,		(b) of lanthanide contraction
	(c) $d$ electrons in Fe . $\square$ (d) $p$ electrons in Cl <sup>-</sup> (at. no. of Cl = 17)		(c) of actinide contraction
10	(a) P		(d) both belong to same transition series
10.	The maximum number of unpaired electrons are in:	22.	
	(a) $Fe^{2+}$		2+
	(c) Fe <sup>4+</sup>		
	(c) 10 L (d) 10 L	1	(c) $Ti^{2+}$ $\Box$ (d) $V^{2+}$ $\Box$

23.	The yellow colour of chromates changes to orange on acidification due to formation of:	36.	The effect of mineral acids on the coinage metals: (a) decreases from Cu to Au	
	2.		(b) increases from Cu to Au	
	•		(c) remains the same  (d) cannot be predicted	
	(c) $\operatorname{Cr}_2\operatorname{O}_7^{2-}$	37.		
24.	Manganese shows oxidation states from +2 to +7. The most	37.	(a) magnesium	
	oxidising state known in aqueous solution is:		(c) aluminium	
	(a) +7	38.	Copper is extracted from sulphide ore using the method:	
	(c) +3	56.	(a) carbon reduction	
25.	What is the magnetic moment of $K_3[FeF_6]$ ?		(b) carbon monoxide reduction	
	[J.E.E. (Orissa) 2005]		(c) auto reduction	
	(a) 5.91 B.M.	39.	• •	
	(c) 3.87 B.M.	39.	In the extraction of copper from copper pyrites, iron removed as:	115
	[Hint: Fe <sup>3+</sup> E.C. = 2, 8, 8 +5, $\mu = \sqrt{5 \times 7} = 5.91$ B.M.]			
26.	Which of the following is an acidic oxide?		(a) $FeSO_4$	
	(a) $Mn_2O_7$	40	(c) $Fe_3O_4$	
	(c) MnO $\square$ (d) Mn <sub>2</sub> O <sub>3</sub> $\square$	40.	**	
27.	Which one of the following ions is diamagnetic?		(a) a mixture of impure copper and silver	
:	(a) $\operatorname{Cr}^{2+}$ (b) $\operatorname{V}^{2+}$		(b) present in the anodic mud in an electrolytic process	
	(c) $\operatorname{Sc}^{3+}$ $\square$ (d) $\operatorname{Ti}^{3+}$ $\square$		(c) electrolytically refined copper	
28.	Transition metals:	41	(d) copper containing about 2% impurity	
	(a) exhibit inert pair effect $\Box$	41.	The flux used in the smelting of copper ores is:	
	(b) have low melting point		(a) limestone	
	(c) do not show catalytic activity	40	(c) silica	
	(d) exhibit variable oxidation states	42.	In the extraction of copper, metal is formed in the Besser	mer
29.	A metal ion from the first transition has a magnetic moment		converter due to reaction:	_
	(calculated) of 3.87 B.M. How many unpaired electrons are	}	(a) $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$	님
	expected to be present in the ion?		(b) $Cu_2S \longrightarrow 2Cu + S$	
	(a) 1		(c) Fe + $Cu_2O \longrightarrow 2Cu + FeO$	
	(c) 3		(d) $2Cu_2O \longrightarrow 4Cu + O_2$	
30.	Coinage metals are:	43.	High purity copper metal is obtained by:	_
	(a) normal elements		(a) carbon reduction   (b) hydrogen reduction	
	(b) transition elements	١.,	(c) electrolytic reduction (d) thermite reduction	
	(c) active elements	44.	The melting points of Cu, Ag and Au follow the order:	_
	(d) highly electropositive elements		(a) $Au > Ag > Cu$	
31.	The position of Cu, Ag and Au in the periodic table is in		(c) $Cu > Ag > Au$ $\Box$ (d) $Ag > Au > Cu$ ,	
	between:	45.		_
	(a) alkali and alkaline earth metals	,	(a) to remove moisture and volatile impurities	
	(b) alkali metals and halogens		(b) to oxidise free sulphur	
	(c) VIII group and zinc metals		(c) to decompose pyrites into Cu <sub>2</sub> S and FeS	
	(d) alkaline earth metals and halogens		(d) for all of the above	<u> </u>
32.	Coinage metals show:	46.	In the electrolytic refining of copper, Ag and Au are fou	
	(a) only monovalency $\Box$ (b) only divalency $\Box$		(a) on cathode $\Box$ (b) on anode	
	(c) only trivalency $\Box$ (d) variable valency $\Box$		(c) in the anodic mud $\Box$ (d) in the cathodic mud	
33.	is the best conductor of electricity.	47.	11	_
	(a) Silver		(a) brass	
	(c) Gold	1	(c) german silver	
34.	The electrons present in the penultimate orbit of coinage	48.	Brass is an alloy containing:	_
	metal atoms are:		(a) Cu and Zn	
	(a) 8		(c) Zn and Sn	
	(c) 18	49.		_
35.	When copper is placed in the atmosphere for sufficient time,		(a) Cu and Al	
	a green crust is formed on its surface. The composition of		(c) Cu, Sn and Zn	
	the green crust is:	50.		_
	(a) $Cu(OH)_2$ $\Box$ (b) $CuO$ $\Box$		(a) $CuO$	
	(c) $CuCO_3$		(c) $CuO_2$ $\Box$ (d) $Cu_2O_2$	

51.	-	eated with metallic copper an	1	66.	Silver can be separated from lead by:	
	HCl, a colourless solut	ion is obtained because of	the for-		(a) fractional crystallisation	
	mation of:		ĺ		(b) amalgamation	
	(a) CuCl <sub>2</sub>	$\square$ (b) $Cu_2Cl_2$			(c) filtration $\Box$ (d) addition of zinc	
	(c) H[CuCl <sub>2</sub> ]	☐ (d) H[CuCl <sub>3</sub> ]		67.	Silver sulphide dissolves in sodium cyanide solution to fo	rm
52.	·CuSO <sub>4</sub> ·5H <sub>2</sub> O is called:	•	1		the complex:	
	(a) green vitriol	☐ (b) blue vitriol			(a) $Na_2[Ag(CN)_4]$	
	(c) white vitriol	☐ (d) gypsum			(c) $Na_3[Ag(CN)_4]$ $\square$ (d) all of these	
53.	In the reaction,			68.	Red precipitate is obtained when silver nitrate is added	to:
		$\longrightarrow A + H_2SO_4 + 2HCl; A is:$	:		(a) $K_2CrO_4$ $\Box$ (b) KI	
	(a) Cu <sub>2</sub> Cl <sub>2</sub>	□ (b) Cu			(c) KBr $\square$ (d) Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	
	(c) CuSO <sub>4</sub>	(d) CuS		69.	Photographic films or plates have as an essent	tial
54.		CuSO <sub>4</sub> and KI, a white preci			ingredient.	
٠		te has the composition:			(a) silver oxide	
	(a) CuI <sub>2</sub>	☐ (b) Cu <sub>2</sub> I			(c) silver thiosulphate $\Box$ (d) silver nitrate	
	(c) KCuI <sub>2</sub>	$\square  \text{(d) } Cu_2I_2$		70.	Percentage of gold in 14 carat gold is:	
55	•	melting copper pyrites with c				
55.		[B.V.(Pun			(c) 40	
	(a) FeS + ZnS		C) 2000)	71.	Silver nitrate is usually supplied in coloured bottles becau	use
	(c) $CuS + FeS_2$	$\Box  (b) \ Cu_2b + Cu_3$			it is:	
56.	<del>-</del>	brass, bronze and german silv	1		(a) oxidised in air	
50.	(a) Cu	(b) Mg	VCI 13.		(b) decomposes in sunlight	
	(c) Al	$\Box  (b) \text{ Mg}$ $\Box  (d) \text{ Zn}$	<u> </u>		(c) explodes in sunlight	
57	* *	ves in excess of KCN to giv			(d) reacts with air in sunlight	
5,,	Copper surprime dissor		E. 2006]	72.	Verdigris is:	
	(a) [Cu(CN) <sub>4</sub> ] <sup>3</sup> -	$\square  \text{(b) } [\text{Cu(CN)}_4]^{2-}$			(a) basic copper acetate $\Box$ (b) basic lead acetate	
	(c) Cu(CN) <sub>2</sub>	(d) CuCN			(c) basic lead	
58.	· · · · · · · · · · · · · · · · · · ·	per sulphate, the metal used to	recover	73.	In solid copper sulphate, copper is coordinated to:	
	copper, is:	•			(a) five water molecules $\Box$ (b) four water molecules	
	(a) Na	□ (b) Ag			(c) one sulphate ion $\Box$ (d) one water molecule	
	(c) Hg	☐ (d) Fe		74.	While extracting an element from its ore, the ore is grou	
59.	Argentite is an ore of:				and reacted with dilute KCN solution to form a solu	ıble
	(a) Ag	□ (b) Au			complex. The element is:	
	(c) Pt	□ (d) Cu			(a) lead	
60.	Cyanide process is use			75	(c) manganese	
	(a) Cr	□ (b) Ag		13.	Percentage of silver in the alloy german silver, is:	
	(c) Cu	$\Box$ (d) Zn			(a) 2.5%	
61.	On heating $Cu(NO_3)_2$ s	strongly, the material finally	obtained	76	(c) 10%	ш
	is:			/0.	(a) red lead	
	(a) Cu	☐ (b) Cu <sub>2</sub> O			(b) ammonical silver nitrate	
(0	(c) Cu(NO <sub>2</sub> ) <sub>2</sub>	$\square$ (d) Cu(NO <sub>3</sub> ) <sub>2</sub>		,	(c) ammonical AgNO <sub>3</sub> + red lead	
62.	•	ed to copper sulphate solution	on, blue		(d) ammonical AgNO <sub>3</sub> + red lead + HCHO	$\overline{\Box}$
	colour is obtained due	*	_	77.		ium
	(a) Cu <sup>2+</sup>	$\Box$ (b) Cu(NH <sub>4</sub> SO <sub>4</sub> ) <sub>2</sub>		'''	thiosulphate solution (hypo solution) is added to sil	
	(c) $[Cu(NH_3)_4]^{2+}$	$\Box$ (d) Cu(OH) <sub>2</sub>			bromide is: [E.A.M.C.E.T. 20	
63.	An alloy which does r				(a) $Ag_2S_2O_3$ $\square$ (b) $Ag_2S$	
	(a) solder	☐ (b) bell metal				
	(c) bronze	☐ (d) brass		70	(c) $Ag_3[Na(S_2O_3)_2]$	
64.				78.	German silver has: [D.C.E. 20	
	(a) AgNO <sub>3</sub>	$\Box  \text{(b) } \text{Cu}_2\text{Cl}_2$			(a) Zn	님
سدر	(c) CuCl <sub>2</sub>	(d) Hg <sub>2</sub> Cl <sub>2</sub>		70	(c) Ni	. 🗆
65.	Hair dyes contain:	[V.I.T.E.E		79.	, 11	_
	(a) copper nitrate	☐ (b) gold chloride			(a) CuO	
	(c) silver nitrate	$\Box$ (d) copper sulphate		1	(c) $Cu_2O_2$	لـــا

00	C'1 ' C' 11 11		erest.		1 0=				
80.	Silver is refined by cupell	ation p	rocess. The process rem	oves	95.	The liquid metal at room		•	
	the impurity of:		L. \ A	_		(a) Ca		(b) Zn	
	(a) Cu		b) Au		06	(c) Hg		(d) Pb	
	(c) Pb		d) Pt		96.	Cinnabar is the ore of:		d) <b>d</b> 1	<del></del>
81.	Which is least soluble in					(a) Zn		(b) Cd	
	(a) AgCl		b) AgBr		07	(c) Hg		(d) Ag	
	(c) AgI		d) Ag <sub>2</sub> S		97.	Chemically philosopher's			
82.	The compound soluble in			,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		(a) ZnO		(b) BaO	
	(a) Cu(OH) <sub>2</sub>		b) Al(OH) <sub>3</sub>		00	(c) HgCl		(d) Hg <sub>2</sub> Cl <sub>2</sub>	. 🗆
	(c) Cr(OH) <sub>3</sub>		d) Fe(OH) <sub>3</sub>		98.	Philosopher's wool wher	nea	ted with BaO at 1100°C	gives
83.	AgCl on fusion with sod					the compound:		(L) D . (7.0)	
	(a) $Ag_2CO_3$		b) Ag <sub>2</sub> O		-	(a) BaCdO <sub>2</sub>		(b) Ba + $ZnO_2$	
	(c) Ag		d) $Ag_2C_2$		00	• •		(d) BaZnO <sub>2</sub>	
84.	Which metallurgy involv	es leac	ching? [D.C.E. 2	2006]	99.	The purest zinc is made		a) 16 th	_
	(a) Au		b) Ag			(a) Zone refining		(b) Mond's process	
	(c) both (a) and (b)	, D (	d) none of these		100	(c) Poling process			
85.	Gold is soluble in:	v			100.	A compound is yellow w	nen	not and white when cold	. The
	(a) conc. HCl		b) conc. H <sub>2</sub> SO <sub>4</sub>			compound is:		43 PLO	-
	(c) conc. HNO <sub>3</sub>		d) aqua-regia			(a) $Al_2O_3$		(b) PbO	
86.	Amongst the following, to	he low	est degree of paramagne	etism	101	(c) CaO		(d) ZnO	
	per mole of the compour	ıd will	be shown by:		101.	The hydroxide which is s	solub	ie in excess of NaOH soi	ution
	(a) MnSO <sub>4</sub> ·4H <sub>2</sub> O		b) CuSO <sub>4</sub> ·5H <sub>2</sub> O			is:		do recorn	-
	(c) FeSO <sub>4</sub> ·7H <sub>2</sub> O	<u> </u>	d) NiSO <sub>4</sub> ·6H <sub>2</sub> O			(a) Cu(OH) <sub>2</sub>		(b) Fe(OH) <sub>3</sub>	
87.	Identify the statement wh	ich is 1	not correct regarding Cu	SO <sub>4</sub> .	100	(c) Cr(OH) <sub>3</sub>		(d) $Zn(OH)_2$	
	(a) It reacts with KI to g	ive iod	line		102.	The colour of zinc sulph			-
	(b) It reacts with NaOH	and gl	ucose to give Cu2O	. 🗆		(a) yellow		(b) white	
	(c) It reacts with KCl to	_			100	(c) brown		· /	
	(d) It gives CuO on stro				103.	The compound which is	wic	iery used as a write pig	ment,
88.	What is the effect of sh			small		is:	_	(h) A1 ()	
	quantity of anhydrous C					(a) PbCO <sub>3</sub>		(b) $Al_2O_3$	
	(a) The white solid dissol	-		on 🗆	101	(c) ZnO		(d) CaCO <sub>3</sub>	
	(b) The white solid disso				104.	Corrosive sublimate is:			
	(c) The white solid disso					(a) HgCl <sub>2</sub>		(b) $Hg_2Cl_2$	
	(d) The white solid turn					(c) Hg <sub>2</sub> Cl		(d) $Hg_2Cl_3$	
89.	When copper reacts with				105.	Calomel is the name of:			
			[A.F.M.C.			(a) HgCl <sub>2</sub>		(b) Hg <sub>2</sub> Cl <sub>2</sub>	
	(a) H <sub>2</sub>		(b) SO <sub>2</sub>			(c) HgCl <sub>2</sub> + Hg		(d) $Hg_2Cl_2 + Hg$	· 🗆
	(c) O <sub>2</sub>		(d) N <sub>2</sub>		106.	Which of the following	com	pound is used as a purga	tive?
90.	Which silver halide is le		· · · · · · · · · · · · · · · · · · ·			(a) Cu <sub>2</sub> Cl <sub>2</sub>			
,	(a) AgF		(b) AgCl			(c) Hg <sub>2</sub> Cl <sub>2</sub>		(d) HgCl <sub>2</sub>	
	(c) AgBr		(d) AgI		107.	In the reaction, SnCl <sub>2</sub> +		· · · · · · · · · · · · · · · · · · ·	
91.	AgCl precipitate dissolve		. , .		10	(a) Hg <sub>2</sub> Cl <sub>2</sub>	_	(b) Hg	
	(a) $Ag(NH_3)_2Cl$		(b) Ag(NH <sub>4</sub> ) <sub>2</sub> Cl					(d) HgCl <sub>3</sub>	
	(c) $Ag(NH_4)_2OH$		(d) Ag(NH <sub>3</sub> ) <sub>2</sub> OH		100	(c) HgCl			ليا .
92.	- 1 1 4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			_	108.	In the reaction, HgCl <sub>2</sub> +		•	_
,, 200	(a) Parkes process		(b) Solvay process			(a) HgI <sub>2</sub>		(b) $K_2HgI_3$	
	(c) cyanide process		(d) amalgamation proce			(c) $K_2HgI_4$		(d) KHgI <sub>3</sub>	
03	Zinc is a member of IIB				109.		oitate	d from zinc sulphate so	lution
7.).	The other members of the			iauic.		by the addition of:			
	(a) boron and aluminium	_	-	rs, 🗆		(a) Na <sub>2</sub> CO <sub>3</sub>		(b) CaCO <sub>3</sub>	
•	(c) silver and gold		(d) tin and lead	ıy 🗆		(c) MgCO <sub>3</sub>		(d) NaHCO <sub>3</sub>	
Q <sub>4</sub>	Calamine is the ore of:	· · ·	(a) un and read		110.		foll	owing sublimes on heating	ng, is:
74.	(a) Zn		(b) Pb			(a) HgCl <sub>2</sub>		,	
	(c) Ca		(d) Hg			(c) $Zn(NO_3)_2$			
	(v) cu		(~) **5		ŀ	3/2		\-/04Z	

111.	Which of the following is insoluble in cold water?			(iii) Acquires yellow colour on heating	
	[A.I.I.M.S. 20	04]		(a) ZnO $\Box$ (b) Al <sub>2</sub> O <sub>3</sub>	
	(a) $Hg_2(NO_3)_2$			(c) PbO	
	(c) $Hg(NO_3)_2$		125.	When excess of SnCl <sub>2</sub> is added to a solution of HgCl <sub>2</sub>	<sub>2</sub> , a
112.	In Nessler's reagent the active ion is:	,		white precipitate turning to grey, is obtained. The g	rey
	(a) $Ag^+$			colour is due to the formation of:	-
	(c) $HgI_3^{2-}$			(a) $Hg_2Cl_2$ $\Box$ (b) $SnCl_4$	
113.	Sulphide ore of zinc is concentrated by:			(c) Sn	
	(a) froth floatation		126.	Essential constituent of an amalgam is:	
	(b) electromagnetic process			(a) iron	
	(c) gravity process			(c) silver	
	(d) distillation		127.	Nessler's reagent is:	_
114.				(a) $K_2HgI_4$	
~~	(a) $ZnS$ $\Box$ (b) $ZnSO_4$			(c) $K_2HgI_2 + KOH$ $\Box$ (d) $K_2HgI_4 + Hg$	
	(c) $ZnSO_4 \cdot 7H_2O$ $\Box$ (d) $ZnCO_3$		128	If NaOH is added to an aqueous solution of zinc ion	_
115.	Granulated zinc is made by :	_	120.	white precipitate appears and on adding excess NaOH,	
113.	(a) pouring molten metal in water	- 🖂 - 🖂		precipitate dissolves. In this solution zinc exists in the	
	(b) pouring molten metal in molten nickel		-	(a) cationic part	
	(c) displacing zinc from a ZnSO <sub>4</sub> solution			(b) anionic part	
	(d) zone refining			(c) both in cationic and anionic parts	
116.	On heating $ZnCl_2 \cdot 2H_2O$ , the compound obtained is:			(d) there is no zinc in solution	
110.	(a) $ZnCl_2$		129.	The formula of haematite is:	ш
	- · · · · · · · · · · · · · · · · · · ·		129.		
117	, · · · · · · · · · · · · · · · · · · ·	_			
117.	The compound which is used in the preservation of we	oou	130.	., .	
	is:		150.	The atomic number of iron is 26. The electronic co	1111-
	(a) NaCl			guration is:	_
110	(c) ZnCl <sub>2</sub>			(a) 2, 8, 8, 8	
118.	Mercury is transported in the containers made of:	_	121	(c) 2, 8, 13, 3	
	(a) Ag		131.		_
110	(c) Al			(a) normal element	
119.	Lucas reagent is:	_		(b) representative element	
	(a) $ZnCl_2 + HCl(conc.)$ $\Box$ (b) $MnO_2 + H_2O$			(c) transition element	
100	(c) $H_2SO_4 + HCl$ $\Box$ (d) $NO + H_2O$		100	(d) inner-transition element	
120.	Mercury on heating with aqua-regia gives:		132.	Which one of the following statements is not correct?	_
	(a) $Hg(NO_3)_2$			(a) Iron belongs to VIII group	
101	(c) $Hg(NO_2)_2$ $\square$ (d) $Hg_2Cl_2$			(b) Iron belongs to third period	
121.	Which one of the following statements is wrong?	_	1	(c) Iron is the member of 3 <i>d</i> -series	
	(a) HgCl <sub>2</sub> dissolves in hot water			(d) Iron is a transition metal	
	(b) HgCl <sub>2</sub> gives HCl when treated with sulphuric acid		133.		_
	(c) HgCl <sub>2</sub> gives yellow ppt. with NaOH			(a) haematite	
	(d) HgCl <sub>2</sub> gives white ppt. with ammonium hydroxide			(c) iron pyrites $\square$ (d) chalcopyrites	
122.	Which one of the following statements is correct?		134.	The iron ores are concentrated by:	_
	(a) Hg <sub>2</sub> Cl <sub>2</sub> is called corrosive sublimate			(a) gravity separation	
	(b) Hg <sub>2</sub> Cl <sub>2</sub> gives white ppt. with ammonium hydroxide			(b) froth floatation process	
	(c) Hg <sub>2</sub> Cl <sub>2</sub> is used as a purgative			(c) amalgamation $\Box$ (d) hand picking	
	(d) Hg <sub>2</sub> Cl <sub>2</sub> is soluble in water		135.	The materials mixed before the calcined ore is subjected	l for
123.	Mark the correct statement:			smelting in the extraction of iron are:	
	(a) Hg forms an amalgam with iron			(a) coke and silica	
	(b) Hg vapour is non-poisonous			(b) coke and limestone	
	(c) Hg is monovalent in mercurous compounds			(c) limestone and silica	
	(d) Oxysalts of mercury are thermally unstable			(d) coke, limestone and silica	
124.	Which of the following oxides has the follow	ving	136.	The smelting of iron in a blast furnace involves all	the
	characteristics?	_		following processes, except:	
	(i) Amphoteric nature			(a) combustion $\Box$ (b) reduction	
	(ii) Can be reduced by carbon			(c) slag formation $\Box$ (d) sublimation	

137.	The maximum temperatu	re 15	600°C is obtained in the		153.	FeSO <sub>4</sub> ·7H <sub>2</sub> O is known a	s:	•	
	region of the blast furnac					(a) green vitriol		(b) white vitriol	
	(a) reduction		(b) fusion			(c) blue vitriol		(d) vitriol	
	(c) combustion		(d) slag formation		154.	Acidified potassium per	mang	ganate is decolourised by:	
138.	In the extraction of iron			cing		(a) white vitriol		(b) bleaching powder	
	agent for the ore is:		·	•		(c) laughing gas		(d) Mohr's salt	
	(a) carbon	$\Box$	(b) carbon monoxide		155.	Number of unpaired elec			
	(c) carbon dioxide		(d) silica			(a) zero			
139.	The iron obtained from t		• •			(c) 4		(d) 5	
	(a) pig iron		(b) cast iron		156.		lding	potassium iodide solutio	n to
	(c) wrought iron		(d) steel			a solution of:		, 1	
140.	Purest form of iron is:		( )			(a) ZnCl <sub>2</sub>		(b) FeCl <sub>3</sub>	
	(a) pig iron		(b) cast iron			(c) HgCl <sub>2</sub>		(d) AlCl <sub>3</sub>	
	(c) wrought iron		(d) steel		157.	Mohr's salt is a:		()	
141.	The carbon content in st		• •			(a) normal salt		(b) acid salt	
	(a) 0.21 to 0.25%		(b) 2 to 2.5%			(c) basic salt		(d) double_salt	
	(c) 0.25 to 2%		(d) 5 to 8%		158.			produced when ferric chlo	oride
142.	Stainless steel contains					solution is treated with:			77. 2
~,	(a) Zn		(b) Cu			(a) KSCN		(b) KCN	
	(c) Al		(d) Cr		ļ	(c) K <sub>4</sub> Fe(CN) <sub>6</sub>		(d) K <sub>3</sub> Fe(CN) <sub>6</sub>	
143.	* *		immersed in water, the		159.			compound is formulated	
	becomes:		·		10).	$[Fe(H_2O)_5(NO)]SO_4$ . Th			
	(a) soft and malleable		(b) hard and brittle			(a) 1		(b) 0	
	(c) tough and ductile		(d) fibrous			(c) 2		(d) 3	
144.			s of iron embedded in char	coal	160.	Ferrous sulphate on he		` '	
1	powder. The process is	-		Cour	100.	(a) $SO_2$ and $SO_3$			
	(a) tempering		(b) annealing			(c) $SO_3$ only		(d) $SO_2$ and $O_2$	
	(c) hardening		(d) case hardening		161.			combines with $Fe^{2+}$ ion to	
145.	Iron is rendered passive				101.	a brown complex?	mg c	onionies with real on to	IOIII
2 101	(a) $H_2SO_4$ (dil.)	-	(b) H <sub>3</sub> PO <sub>4</sub>			(a) N <sub>2</sub> O		(b) NO	
	(c) HNO <sub>3</sub> (conc.)		(d) HCl			(c) $N_2O_3$		(d) N <sub>2</sub> O <sub>5</sub>	
146.			ting steel in atmosphere of		162.	Finely divided iron com			Ц
110.	(a) ammonia		(b) oxygen	, 	102.	(a) Fe(CO) <sub>5</sub>		<del>-</del> ·	
	(c) carbon dioxide		• •			(c) Fe <sub>3</sub> (CO) <sub>12</sub>		- · · · · · · · · · · · · · · · · · · ·	
147.			hen limestone is added to		163.	Bessemer converter is a			اـــا
~	blast furnace, the calcium				105.	(a) pig iron		(b) steel	
	(a) slag		(b) gangue			(c) wrought iron		(d) cast iron	
	(c) metallic calcium		(d) calcium carbonate		164				ч
148.	Annealing process is:		(a) barbarir barborimio		164.	(a) red		(b) blue	
,		ht re	d and then cooling sudder	ılv□		(c) white		, ,	
	-		ed and then cooling slow	-	165.	In our country, iron is		· · ·	
	(c) heating the rods of i			-, <u> </u>	105.	(a) cassiterite			
	(d) heating the rods of is					(c) haematite		* *	
149.	Which one of the metals				166.	* *		g elements constitutes a r	
2 17.	(a) Zn		(b) Ag		100,		wiiiş	g elements constitutes a n	najoi
	(c) Cu		(d) Fe			impurity in pig iron?	_	(h) O	
150.	Rust is:	lumi	(d) 10	Lund		(a) Graphite		( )	
100.	(a) $Fe_2O_3$		(b) FeO·xH <sub>2</sub> O		167	(c) Sulphur			_
	(c) $Fe_2O_3 xH_2O$		• •		167.		gis	the correct IUPAC name	6 101
151.			red hot iron, the substa			K <sub>4</sub> Fe(CN) <sub>6</sub> ?	:da		
1.71,	formed are:	J • C1	. The mon, the substi			(a) Potassium ferricyan			
	(a) $Fe_2O_3 + H_2$	П	(b) $Fe_3O_4 + H_2$			(b) Potassium ferrocyan		rota (II)	
	(c) FeO + H <sub>2</sub>		- · · · -			(c) Potassium hexacyan			
152.	Iron is obtained on a lar			<b></b>	160	(d) Potassium hexacyan			
1.04.	(a) reduction with Al	ge 3			168.		iron	from haematite, limesto	ne is
	(a) reduction with II	ㅁ	• •		1	added to act as:			

	(a) slag	$\Box$ (b) an oxidising agent		182.		g metals exhibit more than	one
1.00	(c) a reducing agent	☐ (d) flux			oxidation state?		
169.		statements is not true for M	ohr's		(a) Na	□ (b) Mg	
	salt?		_		(c) Fe	☐ (d) All	
	(a) It decolourises KMn0	O <sub>4</sub> solution		183:		dium, etc., are called nobel m	etals
	(b) It is a double salt				because:		
	(c) Oxidation state of iro	n is +3			(a) Alfred Nobel discovery	ered them	
	(d) It is a primary standa	ŗd		,	(b) they are inert toward	ls many common reagents	
170.	When K <sub>4</sub> Fe(CN) <sub>6</sub> is adde	d to FeCl <sub>3</sub> , the complex comp	ound		(c) they are shining, lus	trous and pleasing to look at	
	formed is:				(d) they are found in na		
	(a) $Fe_3[Fe(CN)_6]_4$	$\Box$ (b) Fe <sub>4</sub> [Fe(CN) <sub>6</sub> ] <sub>3</sub>		184.	•		
		$\square \text{ (d) } K_2Fe_3[Fe(CN)_6]_2$				[C.B.S.E. (P,M.T.)	20101
171.		es of ferrous sulphate is in the			(a) $7r^{4+}$ Hf <sup>4+</sup>	$\square \text{ (b) Fe}^{2+}, \text{Ni}^{2+}$	
1,11	(a) manufacture of blue-l				(a) Zr <sup>4+</sup> , Hf <sup>4+</sup> (c) Zr <sup>4+</sup> , Ti <sup>4+</sup>	$\square  (d) \text{ Zn}^{2+}, \text{Hf}^{4+}$	
	(b) manufacture of writing			105			اسما
		-		165.	Permanent magnet is ma		
	(c) manufacture of sulph				(a) cast iron	(b) steel	·
170	(d) manufacture of hydro			406	(c) wrought iron		
1/2.	Ferric sulphate on heating		_	186.	-	s salts, ferric salts are:	
	- · · ·	$\square$ (b) SO <sub>2</sub> only			(a) more stable	☐ (b) less stable	
	(c) $SO_3$ only	$\Box$ (d) S only			(c) equally stable	$\Box$ (d) none of these	
173.	Which of the following n	netals corrodes readily in mois	st air?	187.	The metal which does no	ot react with cold water but ev	olves
	(a) Au	□ (b) Ag			hydrogen with steam is:	:	
	(c) Ni	☐ (d) Fe			(a) Na	□ (b) ⋅ <b>K</b> .	
174.	Which of the following	has lowest percentage of car	bon?		(c) Pt	□ (d) Fe	
	(a) Cast iron	☐ (b) Wrought iron		188.	The iron salt used in bl	ue prints is:	
	(c) Steel				(a) $FeC_2O_4$	$\Box$ (b) Fe <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	
	(d) All have same perce	ntage			(c) $K_4Fe(CN)_6$	$\square  \text{(d) FeSO}_4$	
175.	In the reaction, 4Fe + 30	$O_2 \longrightarrow 4 \text{Fe}^{3+} + 6 \text{O}^{2-}$ ; which of	of the	189.	· · · · · ·		_
	following statements is			109.		s oxidised even on exposure	o air
	(a) It is a redox reaction				is:		_
	(b) Metallic iron is reduce	ced to Fe <sup>3+</sup>			(a) $Co_2(SO_4)_3$	$\square$ (b) NiSO <sub>4</sub>	Ш
	(c) Fe <sup>3+</sup> is an oxidising				(c) FeSO <sub>4</sub>	$\Box$ (d) KMnO <sub>4</sub>	
	(d) Metallic iron is a red			190.	Anhydrous ferric chlori	de is prepared by:	
176.	When AgCl is treated wi		_		(a) dissolving ferric hyd	roxide in dilute HCl	
170.	(a) Ag is precipitated				(b) dissolving ferric hyd	lroxide in conc. HCl	
					(c) by passing dry Cl <sub>2</sub>	gas over heated scrap iron	· 🗆
	(b) double decomposition	ii leaction occurs				gas over heated scrap iron	
	(c) a complex is formed			191.	In the dichromate diani	-	
100	(d) no reaction occurs				(a) 4Cr—O bonds are e		
177.	Which of the following v	vill dissolve in excess of amm		1	(b) 6Cr—O bonds are e	-	
	•	[A.M.U. (Engg.)	2010]		(c) all Cr—O bonds are	-	
	(a) AgI	$\Box$ (b) AgBr			(d) all Cr—O bonds are	-	
	(c) AgCl	$\Box$ (d) None of these		192.	· ·	ving pairs of substances on rea	_
178.		which has highest melting p	ooint:	1,72,	will not evolve H <sub>2</sub> gas?		Ction
	(a) pig iron	☐ (b) cast iron			(a) Iron and dil. H <sub>2</sub> SO <sub>4</sub>		
	(c) steel	☐ (d) wrought iron			(c) Copper and HCl(g)	(b) from and steam	
179.	The most stable oxidation	on state of iron is:		1		look of	
	(a) $+2$	□ (b) +3		102	(d) Sodium and ethyl al		Ш
	(c) $-2$	$\Box$ (d) $-3$		193.	J 2 1	_	<u></u>
180.	7 7	ting it with a thin layer of:			(a) $CrO_4^{2-}$	$\Box  \text{(b) } \text{Cr(OH)}_2$	
	(a) Cu	□ (b) Zn			(c) $Cr_2O_7^{2-}$	$\Box$ (d) Cr(OH) <sub>3</sub>	. 🗆
				194.		added conc. H <sub>2</sub> SO <sub>4</sub> to potati	
101	(c) Pb	$\Box$ (d) Mg			-	aploded due to the formation	of an
181.	Which is not amphoteri		_		explosive. Which of the	e following is formed?	
	(a) $Al_{2}^{3+}$	$\Box$ (b) $\operatorname{Cr}^{3+}$				[A.M.U. (Engg.)	2010]
	· (c) Fe <sup>2+</sup>	$\Box$ (d) $Zn^{2+}$			(a) $Mn_2O_7$	$\Box$ (b) MnO <sub>2</sub>	
	•			I	(c) $Mn_2O_5$	$\Box$ (d) Mn <sub>2</sub> O <sub>3</sub>	_ 🗆

195.	Which one of the ionic species will impart colour to an	206.	The catalytic activity of transition elements and their
	aqueous solution?		compounds is described to: [C.E.E. (Kerala) 2002]
	(a) $Ti^{4+}$ $\Box$ (b) $Cu^{+}$ $\Box$		(a) their chemical reactivity
	(c) $\operatorname{Zn}^{2+}$ $\square$ (d) $\operatorname{Cr}^{3+}$ $\square$		(b) their magnetic behaviour
196.	Addition of high proportions of manganese makes steel		(c) their unfilled $d$ -orbitals
	useful in making rails of rail roads, because manganese:	,	(d) their ability to adopt multiple oxidation states and their
	(a) gives hardness to steel	,	complexing ability
	(b) helps the formation of oxides of iron $\Box$	207.	Which of the following sets is of coinage metals?
	(c) can show highest oxidation state of +7		[D.P.M.T. 2003]
	(d) imparts special colour to steel		(a) Cu, Ag, Au $\Box$ (b) Zn, Cd, Hg $\Box$
197.	Which of the following statements is not correct with		(c) Au, Ag, Zn $\Box$ (d) Li, Na, K $\Box$
	reference to ferrous and ferric ions?	208.	A reduction in the atomic size with increase in atomic number
	(a) Fe <sup><math>3+</math></sup> gives brown colour with potassium ferricyanide $\Box$		is a characteristic of the elements of:
	(b) $Fe^{2+}$ gives blue precipitate with potassium ferricyanide $\Box$		(a) $d$ -block $\square$ (b) $f$ -block $\square$
	(c) Fe <sup>3+</sup> gives red colour with potassium thiocyanate		(c) radioactive series $\Box$ (d) high atomic masses $\Box$
	(d) Fe <sup>2+</sup> gives brown colour with ammonium thiocyanate $\Box$	209.	**
198.	Amongst the following, identify the species with an atom	-	is treated with an excess of dilute nitric acid?
-	in +6 oxidation state: [I.I.T. (S) 2000]		[A.I.E.E.E. 2003]
	(a) $MnO_4^-$		(a) $\operatorname{Cr}^{3+}$ and $\operatorname{Cr}_2\operatorname{O}_7^{2-}$ are formed
	(c) NiF <sub>6</sub> <sup>2</sup> $\Box$ (d) CrO <sub>2</sub> Cl <sub>2</sub> $\Box$		(b) $Cr_2O_7^{2-}$ and $H_2O$ are formed
100			(c) $Cr_2O_7^{2-}$ is reduced to +3 state of Cr
199.	What is the shape of $Fe(CO)_5$ molecule? [C.B.S.E. 2000] (a) Tetrahedral $\Box$ (b) Octahedral $\Box$		(d) $\operatorname{Cr}_2\operatorname{O}_7^{2-}$ is oxidised to +7 state of Cr
	(c) Trigonal bipyramidal (d) Square pyramidal	210.	The atomic numbers of vanadium (V), chromium (Cr),
200.	In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by	210.	manganese (Mn) and iron (Fe) are 23, 24, 25 and 26
200.	iodometry, the equivalent weight of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> is:		respectively. Which one of these may be expected to have
	[I.I.T. (S) 2001]		the highest second ionisation enthalpy? [A.I.E.E. 2003]
			(a) V
	(a) $\frac{\text{Molecular weight}}{2}$		(c) Mn $\square$ (d) Fe $\square$
	<del>-</del>	211.	2.
	(b) $\frac{\text{Molecular weight}}{6}$		values will be closest to the radius of Lu <sup>3+</sup> (At. no. of
	·		Lu = $71$ , La = $57$ )? [A.I.E.E. 2003]
	(c) $\frac{\text{Molecular weight}}{3}$		(a) $1.6 \text{ Å}$
	(d) Same as molecular weight		(c) $1.06 \text{ Å}$
201.	Which one of the following is the correct configuration of	212.	· · · · · · · · · · · · · · · · · · ·
	Fe <sup>3+</sup> ( $Z = 26$ )? [S.C.R.A. 2001]		oxidation state? [C.B.S.E. (Medical) 2003]
	(a) [Ar] $4s^2$ , $3d^6$		(a) Ce
			(c) Nd
202	(c) [Ar] $3d^5$	213.	
202.	Which group contains coloured ions out of:[C.P.M.T. 2001]		follows the order (Atomic no. of $Ti = 22$ , $V = 23$ , $Cr = 24$ ,
	1. $Cu^+$ 2. $Ti^{4+}$ 3. $Co^{2+}$ 4. $Fe^{2+}$		Fe = 26): [C.B.S.E. (Medical) 2003; A.I.I.M.S. 2007]
	(a) $1, 2, 3, 4$		(a) $CrO > VO > FeO > TiO$
***	(c) 2, 3		(b) $TiO > FeO > VO > CrO$
203.	The number of ions formed on dissolving one molecule of		(c) $TiO > VO > CrO > FeO$
	FeSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O is/are: [A.I.I.M.S. 2001]		(d) $VO > CrO > TiO > FeO$
	(a) 6	214.	Vitamin –B <sub>12</sub> contains: [C.B.S.E. (Medical) 2003]
204	(c) 5		(a) $\operatorname{Co}^{3+}$ $\square$ (b) $\operatorname{Zn}^{2+}$ $\square$
204.			(c) $Ca^{2+}$ $\Box$ (d) $Fe^{2+}$ $\Box$
	acts as an oxidising agent to give MnO <sub>2</sub> , Mn <sup>2+</sup> , Mn(OH) <sub>3</sub> ,	215.	Which of the following pairs of ions have same para-
	$MnO_4^{2-}$ are respectively: [A.I.E.E. 2002]		magnetic moment ? [E.A.M.C.E.T. (Engg.) 2004]
	(a) 3, 5, 4 and 1		(a) $Mn^{2+}$ , $Cu^{2+}$ $\Box$ (b) $Cu^{2+}$ , $Ti^{3+}$ $\Box$
205	(-) -, ,		(c) $Ti^{4+}$ , $Cu^{2+}$ $\Box$ (d) $Ti^{3+}$ , $Ni^{2+}$ $\Box$
205.	Which one of the following is an example of non typical transition elements? [P.M.T. (M.P.) 2002]		[Hint: $Cu^{2+}$ E.C. = $3d^9$ -one unpaired electron, $Ti^{3+}$ E.C. = $3d^1$ -
	(a) Li, Na, K • $\Box$ (b) Be, Al, Pb		one unpaired electron.]
	(a) El, Na, K		·

216.	The colourless species is: [A.I.I.M.S. 2003]		(c) H <sub>2</sub> SO <sub>4</sub> is a dibasic acid □
	(a) $VCl_3$ $\Box$ (b) $VOSO_4$ $\Box$		(d) rate is faster in the presence of $H_2SO_4$
	(c) $Na_3VO_4$ $\Box$ (d) $[V(H_2O)_6]SO_4\cdot H_2O$ $\Box$		(e) only $H_2SO_4$ is completely ionised
217.	Lanthanide for which +II and +III oxidation states are	226.	The correct order of ionic radii of Y <sup>3+</sup> , La <sup>3+</sup> , Eu <sup>3+</sup> and Lu <sup>3+</sup>
	common is: [A.I.I.M.S. 2003]		is: [P.M.T. (Kerala) 2007]
	(a) La $\Box$ (b) Nd $\Box$		(a) $Y_{3+}^{3+} < La_{3+}^{3+} < Eu_{3+}^{3+} < Lu_{3+}^{3+}$
	(c) Ce		(b) $Lu_{3+}^{3+} < Eu_{3+}^{3+} < La_{3+}^{3+} < Y_{3+}^{3+}$
218.	How many electrons are involved in reduction of KMnO <sub>4</sub>		(c) $La^{3+} < Eu^{3+} < Lu^{3+} < Y^{3+}$
	in basic medium? [J.E.E. (Orissa) 2003]		(d) $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$
•	(a) 1	207	(e) $Eu^{3+} < La^{3+} < Lu^{3+} < Y^{3+}$
	(c) 5	227.	Excited state of configuration of Mn <sup>2+</sup> is:
219.	Lanthanides and actinides resemble in: [A.F.M.C. 2004]		[A.M.U. (Engg.) 2007]
	(a) electronic configuration		(a) $t_{2g}^4$
	(b) oxidation state $\Box$ (c) ionisation state $\Box$		(c) $t_{2g}^4 e_g^2$
222	(d) formation of complexes	228.	Extraction of zinc from zinc blende is achieved by:
220.	Among the following series of transition ions, the one where		[I.I.T. 2007]
	all metal ions have $3d^2$ electronic configuration is (Atomic		(a) electrolytic reduction
	no. of $Ti = 22$ ; $V = 23$ ; $Cr = 24$ ; $Mn = 25$ ):		(b) roasting followed by reduction with carbon
	[C.B.S.E. (P.M.T.) 2004]		(c) roasting followed by reduction with another metal (d) roasting followed by self reduction
	(a) $\text{Ti}^{3+}$ , $\text{V}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Mn}^{4+}$ $\square$ (b) $\text{Ti}^{+}$ , $\text{V}^{4+}$ , $\text{Cr}^{6+}$ , $\text{Mn}^{7+}$ $\square$	229.	(d) roasting followed by self reduction  A solution of a metal ion when treated with KI gives a red
	(c) $Ti^{4+}, V^{3+}, Cr^{2+}, Mn^{3+}$ $\square$ (d) $Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}$ $\square$	229.	precipitate which dissolves in excess of KI to give a
221.	Lanthanides are: [C.B.S.E. (P.M.T.) 2004]	1	colourless solution. Moreover, the solution of metal ion on
	(a) 14 elements in the sixth period (Atomic number 90 to		treatment with a solution of cobalt (II) thiocyanate gives
	103) that are filling $4f$ -sublevel		rise to a deep blue crystalline precipitate. The metal ion is:
	(b) 14 elements in the sixth period (Atomic number 58 to		[L.I.T. 2007]
	71) that are filling $4f$ -sublevel		(a) $Pb^{2+}$ $\Box$ (b) $Hg^{2+}$ $\Box$
	(c) 14 elements in the seventh period (Atomic number 90 to		(a) $Pb^{2+}$ $\Box$ (b) $Hg^{2+}$ $\Box$ (c) $Cu^{2+}$ $\Box$ (d) $Co^{2+}$ $\Box$
	103) that are filling $5f$ -sublevel	230.	Identify the incorrect statement among the following:
	(d) 14 elements in the seventh period (Atomic number 58 to		[A.I.E.E.E. 2007]
222	71) that are filling 4 <i>f</i> -sublevel		(a) $4f$ and $5f$ -orbitals are equally shielded $\Box$
222.	The product of oxidation of $I^-$ with $MnO_4^-$ in alkaline		(b) d-block elements show irregular and erratic chemical
	medium is: [I.I.T. (S) 2004]		properties among themselves
	(a) $IO_3^-$		(c) La and Lu have partially filled d-orbitals and no other
	(c) $IO^ \square$ (d) $IO_4^ \square$		partially filled orbitals
223.	Consider the ground state of Cr-atom ( $Z = 24$ ). The number	221	(d) The chemistry of various lanthanoids is very similar \( \sum_{\text{N}} \)
	of electrons with the azimuthal quantum numbers $l = 1$ and	251.	Which one of the following ions is the most stable in aqueous solution? [C.B.S.E. 2007]
	2 are respectively: [A.I.E.E.E. 2004]		aqueous solution? [C.B.S.E. 2007] (a) $V^{3+}$ $\Box$ (b) $Ti^{3+}$ $\Box$
	(a) 12 and 4		(c) $\operatorname{Mn}^{3+}$ $\square$ (d) $\operatorname{Cr}^{3+}$ $\square$
224	(c) 16 and 4	232.	Identify the incorrect statement among the following:
224.	Cerium $(Z = 58)$ is an important member of lanthanides. Which of the following statements about cerium is		[C.B.S.E. 2007]
	incorrect? [A.I.E.E. 2004]		(a) Lanthanoid contraction is the accumulation of
	(a) The common oxidation states of cerium are +3 and +4		successive shrinkages
			(b) As a result of lanthanoid contraction, the properties of
	(b) The +3 oxidation state of cerium is more stable than +4		4d-series of the transition elements have no similarities
	oxidation state		with the $5d$ -series of elements
	(c) The +4 oxidation state of cerium is not known in		(c) Shielding power of $4f$ -electrons is quite weak
	solutions		(d) There is a decrease in the radii of the atoms or ions as
	(d) Cerium (IV) acts as an oxidising agent		one proceeds from La to Lu
225.	KMnO <sub>4</sub> is a strong oxidising agent in acid medium. To	233.	3
	provide acid medium H <sub>2</sub> SO <sub>4</sub> is used instead of HCl. This is		B.M.? [P.E.T. (Kerala) 2007]
	because: [P.M.T. (Kerala) 2007]		(a) $Mn^{2+}$
	(a) H <sub>2</sub> SO <sub>4</sub> is stronger acid than HCl		(c) $\operatorname{Cr}^{2+}$ $\square$ (d) $\operatorname{V}^{3+}$
	(b) HCl is oxidised by KMnO <sub>4</sub> to $Cl_2$		(e) $\operatorname{Cr}^{3+}$

234.	When hydrogen peroxide is added to acidified potassium dichromate, a blue colour is produced due to formation of:  [P.E.T. (Kerala) 2007]		of air, its compound $B$ is formed. $B$ reacts with compound $C$ to give compound $D$ with liberation of iodine. Then the metal $A$ , and compounds $B$ , $C$ and $D$ are respectively:
	(a) $CrO_3$ $\Box$ (b) $Cr_2O_3$ $\Box$		[P.M.T. (Kerala) 2008]
	(c) $CrO_5$ $\Box$ (d) $CrO_4^{2-}$ $\Box$		(a) Ti, TiSO <sub>4</sub> , KI and TiI <sub>2</sub> $\Box$
	(e) $Cr_2O_7^{2-}$		(b) Zn, ZnSO <sub>4</sub> , KI and ZnI <sub>2</sub>
235.	• • • • •		(c) Cu, CuSO <sub>4</sub> , KI and Cu <sub>2</sub> I <sub>2</sub> $\square$
<i></i>	dilute aqueous solution of NaCN in the presence of:		
	[LLT. 2008]	1	(4) 54, 545 54, 124 214 5412
	(a) nitrogen		[Hint: Cu: $1s^2, 2s^22p^6, 3s^23p^63a^{10}, 4s^1$ Magnetic moment
	(c) carbon dioxide		corresponds to one electron
	[Hint: $4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4[NaAg(CN)_2] +$		$Cu + H_2SO_4 + \frac{1}{2}O_2 \longrightarrow CuSO_4 + H_2O$
	4NaOH]	1	(B)
236.	Among the following, the coloured compound is:		$2\text{CuSO}_4 + 4\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2 + 2\text{K}_2\text{SO}_4$
	[I.I.T. 2008]	242	
	(a) CuCl $\Box$ (b) $K_3[Cu(CN)_4]$ $\Box$	243.	What is the correct order of spin only magnetic moment of
	(c) $CuF_2$ $\Box$ (d) $[Cu(CH_3CN)_4]BF_4$ $\Box$		$Mn^{2+}$ , $Cr^{2+}$ and $V^{2+}$ ? [A.F.M.C. 2408]
237.	The correct order of decreasing second ionisation enthalpy		(a) $Mn^{2+} > V^{2+} > Cr^{2+}$
	of Ti(22), V(23), Cr(24) and Mn(25) is: [C.B.S.E. 2008]		(c) $Mn^{2+} > Cr^{2+} > V^{2+}$ $\square$ (d) $Cr^{2+} > V^{2+} > Mn^{2+}$ $\square$
	(a) $Mn > Cr > Ti > V$ $\square$ (b) $Ti > V$ $> Cr > Mn \square$		[Hint: Ion E.C. Unpaired electrons Magnetic moment
	(c) $Cr > Mn > V > Ti$ $\Box$ (d) $V > Mn > Cr > Ti$ $\Box$		$V^{2+} [Ar] 3d^3 \qquad 3.86$
	[Hint: The electronic configurations of $M^+$ ions are:		$Cr^{2+}$ [Ar]3 $d^4$ 4 5.0
	$Cr^{+}$ : $1s^{2}$ , $2s^{2}2p^{6}$ , $3s^{2}3p^{6}3d^{5}$ —Stable configuration		$Mn^{2+}$ [Ar]3 $d^5$ 5 5.96 —]
	Mn <sup>+</sup> : $1s^2$ , $2s^22p^6$ , $3s^23p^63d^5$ , $4s^1$ Nuclear charge V <sup>+</sup> : $1s^2$ , $2s^22p^6$ , $3s^23p^63d^3$ , $4s^1$ increases Ti <sup>+</sup> : $1s^2$ , $2s^22p^6$ , $3s^23p^63d^2$ , $4s^1$ ]	244.	Which has maximum paramagnetic character?[D.C.E. 2008]
	$V : 1s^2, 2s^22p^2, 3s^33p^3a^2, 4s^4$ increases		(a) $[Fe(CN)_6]^{4-}$
000			(c) $[Cu(NH_3)_4]^{2+}$ $\Box$ (d) $[Mn(H_2O)_6]^{2+}$ $\Box$
238.	Dipping iron article into a strongly alkaline solution of	245.	Hybridisation, shape and magnetic moment of K <sub>3</sub> [Co(CO <sub>3</sub> ) <sub>3</sub> ]
	sodium phosphate: [V.I.T.E.E.E. 2008]		is: [J.E.E. (Orissa) 2008]
	(a) does not affect the article (b) forms $Fe_2O_3$ : $xH_2O$ on the surface		(a) $d^2sp^3$ , octahedral, 4.9 B.M.
	(c) forms iron phosphate film		(b) $sp^3d^2$ , octahedral, 4.9 B.M.
	(d) forms ferric hydroxide		(c) $dsp^2$ , square planar, 4.9 B.M.
239.	When SCN <sup>-</sup> is added to an aqueous solution containing		(d) $sp^3$ , tetrahedral, 4.9 B.M.
	Fe(NO <sub>3</sub> ) <sub>3</sub> , the complex ion produced is: [V.I.T.E.E.E. 2008]	246.	The spin only magnetic moment value of Cr(CO) <sub>6</sub> is:
	(a) $[Fe(OH_2)_2(SCN)]^{2+}$ $\square$ (b) $[Fe(OH_2)_5SCN]^{2+}$ $\square$		(a) 0
	(c) $[Fe(OH_2)_8(SCN)]^{2+}$ $\square$ (d) $[Fe(OH_2)_2(SCN)]^{6+}$ $\square$		(c) 4.90
	[Hint: $Fe^{3+} + SCN^{-} + 5H_2O \longrightarrow [Fe(OH_2)_2SCN]^{2+}]$		[Hint: In Cr(CO) <sub>6</sub> , no orbital is present which is singly
240			occupied, hence magnetic moment value is zero.
240.	Which one of the following reactions will occur on heating		$Cr(CO)_6$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$
	AgNO <sub>3</sub> above its melting point? [P.E.T. (Kerala) 2008]		
	(a) $2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$	247	Knowing that the chemistry of lanthanoids (Ln) is
	(b) $2AgNO_3 \longrightarrow 2Ag + N_2 + 3O_2$	247.	dominated by its +3 oxidation state, which of the following
	(c) $2AgNO_3 \longrightarrow 2AgNO_2 + O_2$		statements is incorrect? [A.I.E.E. 2009]
	(d) $2AgNO_3 \longrightarrow 2Ag + 2NO + 2O_2$		(a) Because of large size of the Ln(III) ions the bonding in
	(e) $2AgNO_3 \longrightarrow Ag_2O + N_2O_3 + O_2$		its compounds is predominantly ionic in character $\square$
241.	Which of the following pairs of transition metal ions are the	[	(b) The ionic sizes of Ln(III) decrease in general with
	stronger oxidising agents in aqueous solutions?		increasing atomic number
	[P.M.T. (Kerala) 2008]	رياد شايعت	(c) Ln(III) compounds are generally colourless
	(a) $V^{2+}$ and $Cr^{2+}$ $\Box$ (b) $Ti^{2+}$ and $Cr^{2+}$ $\Box$		(d) Ln(III) hydroxides are mainly basic
	(c) $Mn^{3+}$ and $Co^{3+}$ $\Box$ (d) $V^{2+}$ and $Fe^{2+}$ $\Box$	248.	In context with the transition elements, which of the
	(e) $\operatorname{Ni}^{2+}$ and $\operatorname{Fe}^{2+}$	Ì	following statements is incorrect? [A.I.E.E.E. 2009]
242.	A transition metal A has spin only magnetic moment value		(a) In addition to the normal oxidation states, the zero
	of 1.8 B.M. When it is reacted with dilute H <sub>2</sub> SO <sub>4</sub> in presence		oxidation state is also shown by these elements in
		į.	complexes

	(b) In the highest oxidation states, the transition metals	258.	Which of the following oxidation states is the most common
	show basic character and form cationic complexes		among the lanthanoids? [C.B.S.E. (P.M.T.) 2010]
	(c) In the highest oxidation states of the first five transition		(a) 4
	elements (Sc to Mn), all the 4s and 3d electrons are used		(c) 5 $\Box$ (d) 3 $\Box$
	for bonding	259.	Which of the following ions will exhibit colour in aqueous
	(d) Once the $d^{5}$ configuration is exceeded, the tendency to		solution? [C.B.S.E. (P.M.T.) Prel. 2010]
	involve all the $3d$ electrons in bonding decreases $\square$		(a) $La^{3+}(Z = 57)$
	<b>Hint:</b> In higher oxidation states, transition metals show acidic		(c) $Lu^{3+}(Z=71)$
	properties and form anionic complexes.]	260.	Which of the following ions has electronic configuration
249.	The oxidant which is used as an antiseptic is:	200.	[Ar] $d^6$ ? [C.B.S.E. (P.M.T.) Prel. 2010]
	[J.E.E. (W.B.) 2009]		
	(a) $KBrO_3$ $\square$ (b) $KMnO_4$ $\square$		(a) $Ni^{3+}$ $\square$ (b) $Mn^{3+}$ $\square$
•	(c) $CrO_3$ $\square$ (d) $KNO_3$ $\square$		(c) $Fe^{3+}$ $\Box$ (d) $Co^{3+}$ $\Box$
250.	'Electron' is an alloy of: [J.E.E. (W.B.) 2009]	261.	How many hydrogen bonded water molecule(s) are
	(a) Mg and Zn		associated with CuSO <sub>4</sub> ·5H <sub>2</sub> O? [A.M.U. (Engg.) 2010]
	(c) Ni and Zn		(a) 1
251.	The temperature of the slag zone in the metallurgy of iron		
	using blast furnace is: [C.E.T. (Karnataka) 2009]	262.	What is the magnetic moment of Fe <sup>3+</sup> ion in [Fe(CN) <sub>6</sub> ] <sup>3-</sup> ?
	(a) 1500-1600°C		[A.M.U. (Engg.) 2010]
	(c) 800-1000°C □ (d) 1200-1500°C □		(a) 1.73 B.M.
252.	The magnetic moment of a transition metal is $\sqrt{15}$ BM.		(c) Diamagnetic
	Therefore, the number of unpaired electrons present in it	ļ	[Hint: $[Fe(CN)_6]^3 \longrightarrow \uparrow \downarrow \uparrow \downarrow \uparrow \vdots$ : : : :
	is: [C.E.T. (Karnataka) 2009]		
	(a) 4		No. of unpaired electron = 1 $d^2sp^3$ hyb.
	(c) 2		•
253.	Number of unpaired electrons in Mn <sup>3+</sup> is:		$\mu = \sqrt{n(n+2)} = \sqrt{3} = 1.73$ B.M.
	[J.E.E. (Orissa) 2009]	263.	Which of the following is Vaska's compound?
	(a) 2		[A.M.U. (Engg.) 2010]
	(c) 4		(a) $[Ni(PPh_3)Cl_2]$ $\square$ (b) $[Rh(CO)_2Cl]_2$ $\square$
254.			(c) $Trans \operatorname{IrCl(CO)}(PPh_3)_2 \square$ (d) $\operatorname{IrCl(CO)}_2(PPh_3)_2 \square$
	[J.E.E. (Orissa) 2009]	264.	Mark the correct statement(s): [P.E.T. (Kerala) 2010]
	(a) 5.91		1. Manganese exhibits +7 oxidation state
	(c) 3.91	is and in the second	2. Zinc forms coloured ions
255.	Electronic configuration of Cu <sup>2+</sup> is: [J.E.E. (Orissa) 2009]		3. [CoF <sub>6</sub> ] <sup>3</sup> is diamagnetic .
	(a) $[Ar]4s^13d^8$		4. Sc form +4 oxidation state
	(c) $[Ar]4s^23d^7$		5. Zinc exhibits only +2 oxidation state
256.	MnO <sub>4</sub> reacts with Br in alkaline pH to give:	Ciel Service	(a) 1 and 2 $\cdot \Box$ (b) 1 and 5 $\Box$
	[J.E.E. (Orissa) 2009]		(c) 2 and 4
	(a) $BrO_3^-$ , $MnO_2$ $\Box$ (b) $Br_2$ , $MnO_4^{2-}$ $\Box$	recentific	(e) 2 and 5
	(a) $BrO_3^-$ , $MnO_2$	265.	The maximum oxidation state exhibited by actinide ions is:
	[Hint: $2MnO_4^- + Br^- + H_2O \longrightarrow 2OH^- + 2MnO_2 + BrO_3^-$ ]	Marie market	P.E.T. (Kerala) 2010]
257.	The correct order of $E_{M^{2+}/M}^{\circ}$ values with negative sign for	1100000	
	the four successive elements Cr, Mn, Fe and Co is:	liet Edward	$ (c) +7 \qquad \qquad \Box \qquad (d) +8 \qquad \Box $
	[AJEEE 2010]		(e) $+6$
	(a) $Cr > Mn > Fe > Co$ $\Box$ (b) $Mn > Cr > Fe > Co$ $\Box$	266.	Which of the following is a correct statement?
	(c) $Cr > Fe > Mn > Co$ $\Box$ (d) $Fe > Mn > Cr > Co$ $\Box$	Bholodia	[E.A.M.C.E.T. (Engg.) 2010]
	<b>Paint:</b> The values are $E_{\text{Mn}^{2+}/\text{Mn}}^{\circ} = -1.18 \text{ V}; E_{\text{Cr}^{2+}/\text{Cr}}^{\circ} = -0.91 \text{ V};$	and a second	(a) Aqueous solutions of $Cu^+$ and $Zn^{2+}$ are colourless $\square$ (b) Aqueous solutions of $Cu^{2+}$ and $Zn^{2+}$ are colourless $\square$
	win win Cr-/Cr	E	(b) Aqueous solutions of ('u"' and '/n"' are colourless
		# 15 C	
	$E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V} ; E_{\text{Co}^{2+}/\text{Co}}^{\circ} = -0.28 \text{ V} ]$	ion societies in	(c) Aqueous solution of Fe <sup>3+</sup> is green in colour

#### **Set II**: This set contains questions with two or more correct answers.

267.	67. Which of the following statements are correct when a mixture			Select the compounds having metal in zero oxidation state:				
	of NaCl and K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> is gently warmed with conc. H <sub>2</sub> So	O <sub>4</sub> ?		(a) Ni(CO) <sub>4</sub>	$\Box$ (b) $Cr(CO)_6$			
	[I.I.T. 19	998]		(c) Fe <sub>2</sub> (CO) <sub>9</sub>	☐ (d) Co(CO) <sub>6</sub>			
	(a) A deep red vapour is evolved		274.	Mercurous ion can be re	epresented as:			
	(b) The vapour when passed into NaOH solution give	es a		(a) Hg <sup>+</sup>	-			
	yellow solution of Na <sub>2</sub> CrO <sub>4</sub>			(c) $Hg_2^{2+}$	$\Box (d) \operatorname{Hg}^{2+}$			
	(c) Chlorine gas is evolved				are the members of 3 <i>d</i> -series			
	(d) Chromyl chloride is formed			(a) Ti	$\Box  \text{(b) Ag}$	. 🗆		
268.	Which of the following compounds are coloured due	e to		(c) V	☐ (d) Pd			
	charge transfer spectrum?			• •	identify the species with an	atom		
	(a) $K_2Cr_2O_7$			in +6 oxidation state:	, ·			
	(c) $[Fe(H_2O)_5NO]SO_4$ $\square$ (d) $MnO_2$			(a) KMnO <sub>4</sub>	$\Box$ (b) K <sub>2</sub> MnO <sub>4</sub>			
269.				(c) CrO <sub>2</sub> Cl <sub>2</sub>	$\square$ (d) $K_3Cr(CN)_6$			
	A.		277.	Which metals are presen	The second secon			
	(a) Cu <sup>2+</sup>			(a) Cu	□ (b) Ni			
270.	Transition metal ions form coloured compounds due to	o:		(c) Zn	$\Box$ (d) Ag			
	(a) d-d transition		278.	Transition elements with	4s <sup>1</sup> configuration are:			
	(b) charge transfer spectrum			(a) Cr	□ (b) Mn			
	(c) variable oxidation state			(c) Ni	□ (d) Cu			
	(d) partially filled d-orbitals		279.	The complex forming ten	dency of a transition metal de	pends		
271.	Catalysts used in contact process of manufacture	of		upon:				
	sulphuric acid are:			(a) availability of a num				
	(a) $NO(g)$ $\square$ (b) $V_2O_5$			(b) high ionisation energ				
	(c) Mo			•	on or high charge density			
272.	Oxides of which of the following metals show oxidation s	state	280.	(d) variable oxidation stated the correct stated	•			
	of +8?		200.	(a) Iron is the most abu				
	(a) Ru			(b) Cast iron is the pure				
	(c) Mn			(c) The most stable oxid				
			i	(d) Iron does not form a	· · · · · · · · · · · · · · · · · · ·			

A	nswe	rs																	
1.	(a)	2.	(b)	3.	(c)	4.	(a)	5.	(c)	6.	(d)	7.	(a)	8.	(b)	9.	(d)	10.	(b) ·
11.	(c)	12.	(a)	. 13.	(d)	14.	(c)	15.	(b)	16.	(d)	17.	(a)	18.	(b)	19.	(c)	20.	(d)
21.	(b)	22.	(b)	23.	(c)	24.	(a)	25.	(a)	26.	(a)	27.	(c)	28.	(d)	29.	(c)	30.	(b)
31.	(c)	32.	(d)	33.	(a)	34.	(c)	35.	(d)	36.	(a)	37.	(b)	38.	(c)	39.	(b)	40.	(d)
41.	(c)	42.	(a)	43.	(c)	44.	(b)	45.	(d)	46.	(c)	47.	(b)	48.	(a)	49.	(c)	50.	(b)
51.	(c)	52.	(b)	53.	(a)	54.	(d)	55.	(b)	56.	(a)	57.	(a)	58.	(d)	59.	(a)	60.	(b)
61.	(b)	62.	(c)	63.	(a)	64.	(a)	65.	(c)	66.	(d)	67.	(b)	68.	(a)	69.	(b)	70.	(a)
71.	(b)	72.	(a)	73.	(b)	74.	(d)	75.	(d)	76.	(d)	77.	(d)	78.	(d)	79.	(a)	80.	(c)
81.	(d)	82.	(a)	83.	(c)	84.	(c)	85.	(d)	86.	(b)	87.	(c)	88.	(c)	89.	(b)	90.	(d)
91.	(a)	92.	(a)	93.	(b)	94.	(a)	95.	(c)	96.	(c)	97.	(a)	98.	(d)	99.	(a)	100.	(d)
101.	(d)	102.	(b)	103.	(c)	104.	.(a)	105.	_(b)	106.	_(c)_	107.	(b)	108.	(c)	109.	(d)	110.	
111.	(b)	112.	(d)	113.			(c)	115.	(a)	116.	(b)	117.	(e)	118.	(d)——	119.	–(a)	120.	(b)
121.		122.	(c) -	123.	•	124.		125.		126.	-	127.		128.		129.		130.	
131.		132.		133.	(a)	134.	(a)	135.	(b)	136.	(d)	137.	(c)	138.	(b)	139.	(a)	140.	
141.		142.	(d)	143.	-	144.		145.		146.	(a)	147.	, ,	148.			(d) .	150.	
151.		152.		153.		154.			(c) .	156.		157.			(a) .	159.		160.	
161.		162.		163.		164.		165.		166.		167.		168.		169.		170.	•
171.		172.		173.		174.		175.		176.		177.		178.		179.		180.	
181.		182.		183.		184.		185.		186.		187.		188.		189.		190.	
191.		192.		193.		194.	` ,	195.		196.		) <del>197</del> .		198.		199.		200.	
201.		202.		203.		204.		205.		206.		207.		208.		209.		210.	
211.		212.		213.		214.		215.		216.		217.		218.		219.		220.	
221.	. ,	222.		223.		224.		225.		226.		227.		228.		229.		230.	
231.		232.		233.		234.		235.		236.		237.		238.		239.		240.	
241.		242.		243.		244.	` '	245.		246.		247.		248.		249.	, ,	250.	
251.		252.	• •	253.		254.		255.		256.		257.		258.		259.		260.	
261.		262.		263.		264.		265.		266.			(a,b,d)		(a,b,c)		(b,c,d)		(a,b,d)
271.	(b,d)	272.	(a,b)	2/3.	(a,b,c,d)	2/4.	(b,c)	275.	(a,c)	276.	(b,c)	277.	(a,b,c)	278.	(a, d)	279.	(a,c)	280.	(a,c,d)



## **Objective Questions for IIT ASPIRANTS**



- + Xe<sup>-</sup> Alkaline medium  $\rightarrow$  MnO<sub>4</sub><sup>2</sup>  $MnO_4$ +Ye Acidic medium +Ze Neutral medium
  - X, Y and Z are respectively:
  - (a) 1, 2, 3
- (c) 1, 3, 5
- (d) 5, 3, 1

[Hint: 
$$MnO_4^- + e^- \xrightarrow{Alk. \text{ med.}} MnO_4^{2-}$$

$$MnO_4^- + 8H^+ + 5e^- \xrightarrow{Acid. med.} Mn^{2+} + 4H_2O$$
  
 $MnO_4^- + 4H_2O + 3e^- \xrightarrow{Neu. med.} Mn^{4+} + 8OH^-$ 

- A metal M which is not affected by strong acids like conc. HNO<sub>3</sub>, conc. H<sub>2</sub>SO<sub>4</sub> and concentrated solutions of alkalies like KOH and NaOH but dissolves in aqua-regia and forms  $MCl_3$  which is used for toning in photography. The metal M is:
  - (a) Ag

(b) Hg

(c) Au

(d) Cu

[Hint: Au is not affected by concentrated acids and strong alkalies. However, it dissolves in aqua-regia forming AuCl<sub>3</sub> which is used for toning in photography.

$$[HNO_3 + 3HCl \longrightarrow NOCl + 2Cl + 2H_2O] \times 3$$

$$[Au + 3Cl \longrightarrow AuCl_3] \times 2$$

$$2Au + 3HNO_3 + 9HCl \longrightarrow 2AuCl_3 + 3NOCl + 6H_2O$$

- The metals present in insulin, haemoglobin and vitamin B<sub>12</sub> are respectively:
  - (a) Zn, Hg, Cr
- (b) Co, Fe, Zn
- (c) Mg, Fe, Co
- (d) Zn, Fe, Co

[Hint: Insulin contains zinc, haemoglobin contains iron and vitamin B<sub>12</sub> contains cobalt.]

- Zinc gives H<sub>2</sub> gas with H<sub>2</sub>SO<sub>4</sub> and conc. HCl but not with conc. HNO3 because:
  - (a) NO<sub>3</sub> ion is reduced in preference to hydronium ion
  - (b) conc. HNO<sub>3</sub> is a weaker acid than conc. H<sub>2</sub>SO<sub>4</sub> and conc.
  - (c) conc. HNO3 acts as a reducing agent
  - (d) zinc is more reactive than H<sub>2</sub>

[Hint: 
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \uparrow$$
  
 $Conc.$ 

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2 \uparrow$$

$$Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2NO_2 \uparrow + 2H_2O$$

$$Conc.$$

NO<sub>3</sub> ion is reduced to NO<sub>2</sub> in preference to H<sub>3</sub>O<sup>+</sup> ion.]

- 'Bordeaux mixture' is used as a fungicide. Its composition
  - (a)  $CaSO_4 + Cu(OH)_2$
- (b)  $CuSO_4 + Ca(OH)_2$
- (c)  $CuSO_4 + CaO$
- (d) CuO + CaO
- A compound of mercury used in cosmetics, in Ayurvedic and Yunani medicines and known as Vermilion is:
  - (a) HgCl<sub>2</sub>
- (b) Hg<sub>2</sub>Cl<sub>2</sub>

(c) HgS

(d) HgI<sub>2</sub>

- 7. An ornament of gold having 87.5% of gold, is of ..... carat.
  - (a) 21
- (b) 18
- (c) 15
- (d) 24

[Hint: Pure gold = 24 carat

$$87.5\% \text{ gold} = \frac{87.5}{100} \times 24 = 21.0 \text{ car at}$$

- 87.5% gold =  $\frac{87.5}{100} \times 24 = 21.0$  carat ] The highest magnetic moment is shown by the transition metal ion with outer electronic configuration:
  - (a)  $3d^2$

(c)  $3d^9$ 

(d)  $3d^5$ 

[Hint: In  $3d^5$  configuration, all the d-orbitals are singly occupied, i.e., it has maximum number of unpaired electrons.]

- Number of moles of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> reduced by one mole of Sn<sup>2+</sup> ions is:
  - (a) 1/3

(c) 1/6

(d) 6

[Hint:  $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$ 3 moles of  $\operatorname{Sn}^{2+}$  ions reduce = 1 mole of  $\operatorname{Cr}_2\operatorname{O}_7^{2-}$ 

= 1 mole of  $K_2Cr_2O_7$ 

1 mole of  $Sn^{2+}$  ions will reduce = 1/3 mole of  $K_2Cr_2O_7$ 

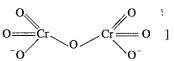
- 10. The reason for the stability of Gd<sup>3+</sup> ion is:
  - (a) 4f-subshell completely filled
  - (b) 4f-subshell empty
  - (c) 4f-subshell half filled
  - (d) possesses the configuration of a noble gas
- 11. Which is the first man-made element?
  - (a) Sc

(b) Tc

(c) Os

- (d) Zr
- **12.** Select correct statement:
  - (a) PH<sub>3</sub> reduces AgNO<sub>3</sub> to metallic Ag
  - (b) Organic tissues turn AgNO3 black by reducing it to Ag
  - (c) AgCN is soluble in KCN
  - (d) All are correct statements
- 13. When K<sub>2</sub>CrO<sub>4</sub> is added to CuSO<sub>4</sub> solution, there is formation of CuCrO<sub>4</sub> as well as CuCr<sub>2</sub>O<sub>7</sub>. Formation of CuCr<sub>2</sub>O<sub>7</sub> is due
  - (a) basic nature of CuSO<sub>4</sub> solution
  - (b) acidic nature of CuSO₄ solution
  - (c) this is the typical property of CuSO<sub>4</sub>
  - (d) there is no formation of CuCr<sub>2</sub>O<sub>7</sub>
- 14. In K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, every Cr is linked to:
  - (a) two O-atoms
- (b) three O-atoms
- (c) four O-atoms
- (d) five O-atoms

**[Hint:** The structure of  $Cr_2O_7^{2-}$  ion is,



- 15. A blue solution of copper sulphate becomes darker when treated with excess of ammonia. This is because:
  - (a) ammonia molecules replace water molecules in the solution
  - (b) ammonia is stronger ligand than water

- (c) ammonia forms a stable complex ion [Cu(NH<sub>1</sub>)<sub>4</sub>]<sup>2+</sup> with Cu<sup>2+</sup> ions
- (d) All are correct

[Hint:

$$\begin{array}{ll} [Cu(H_2O)_4]SO_4 \cdot H_2O + 4NH_4OH & \longrightarrow [Cu(NH_3)_4]SO_4 + 9H_2O] \\ \text{Blue soln.} \end{array}$$

- 16. Sugar in urine-sample can be detected by:

  - (a) Fehling's solution (b) Benedict's solution
  - (c) Tollen's reagent
- (d) all the three (a), (b) and (c)

[Hint: Fehling's soln.—Cu(II) ion (complexed with tartrate ion) is heated in basic solution with a reducing sugar, brick red precipitate of Cu<sub>2</sub>O is formed. Mixture of alk. CuSO<sub>4</sub> and sodium potassium tartrate is called Fehling's solution.

> Benedict's soln.—It contains Cu(II) ion complexed to citrate ion. When it is heated with reducing sugar, Cu(II) is reduced to Cu<sub>2</sub>O.

> Tollen's reagent—Ammonical AgNO3 solution is called Tollen's reagent. Reducing sugars give silver mirror test with Tollen's reagent.

17. In the process of extraction of gold,

Roasted gold ore + 
$$\operatorname{CN}^- + \operatorname{H}_2\operatorname{O} \xrightarrow{\operatorname{O}_2} [X] + \operatorname{OH}^-$$
  
 $[X] + \operatorname{Zn} \longrightarrow [Y] + \operatorname{Au}$ 

Identify the complexes [X] and [Y]:

(a) 
$$X = [Au(CN)_2]^-$$
,  $Y = [Zn(CN)_4]^{2-}$   
(b)  $X = [Au(CN)_4]^3-$ ,  $Y = [Zn(CN)_4]^{2-}$ 

(b) 
$$X = [Au(CN)_4]^{3-}$$
,  $Y = [Zn(CN)_4]^2$ 

(c) 
$$X = [Au(CN)_2]^T$$
,  $Y = [Zn(CN)_6]^4$ 

(c) 
$$X = [Au(CN)_2]^-$$
,  $Y = [Zn(CN)_6]^4$   
(d)  $X = [Au(CN)_4]^{3^-}$ ,  $Y = [Zn(CN)_4]^{2^-}$ 

[Hint: 
$$2Au + 4CN^{-} + H_2O + \frac{1}{2}O_2 \longrightarrow 2[Au(CN)_2]^{-} + 2OH^{-}$$

$$2[Au(CN)_2]^{-} + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Au]$$

- 18. A metal gives two chlorides 'A' and 'B'. 'A' gives black precipitate with NH4OH and 'B' gives white. With KI 'B' gives a red precipitate soluble in excess of KI. 'A' and 'B' are respectively:
  - (a) HgCl<sub>2</sub> and Hg<sub>2</sub>Cl<sub>2</sub>
- (b) Hg<sub>2</sub>Cl<sub>2</sub>, HgCl<sub>2</sub>
- (c) HgCl<sub>2</sub> and HgCl
- (d) none of these

[Hint: 'A' is Hg<sub>2</sub>Cl<sub>2</sub> and 'B' is HgCl<sub>2</sub>.

- **19.** An inorganic compound (A) gave the following reactions:
  - (i) The compound on heating gave a residue and a gaseous mixture of NO2 and O2.

(ii) The aqueous solution of (A) gave a white precipitate with sodium chloride solution. The precipitate dissolves in NH₄OH.

The compound (A) is:

- (a)  $Pb(NO_3)_2$
- (b) Ba(NO<sub>3</sub>)<sub>2</sub>
- (c) AgNO<sub>3</sub>
- (d) none of these

 $2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$ [Hint:

The inorganic compound may be:

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

$$AgNO_3 + NaCI \longrightarrow AgCI + NaNO_3$$
  
 $AgCI + 2NH_4OH \longrightarrow Ag(NH_3)_2CI + 2H_2O]$ 

- 20. An inorganic compound on strong heating gave a blackish brown powder and two oxides of sulphur. The powder was dissolved in HCl when a yellow solution was obtained which gave a blood red coloured solution with thiocyanide ions.
  - (a) CuSO<sub>4</sub>
- (b) ZnSO<sub>4</sub>

- (c) NiSO<sub>4</sub> (d) FeSO<sub>4</sub>

$$Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$$
Yellow

[Hint:  $2FeSO_4 \longrightarrow Fe_2O_3 + SO_2 + SO_3$ 

FeCl<sub>3</sub> + CNS<sup>-</sup> 
$$\longrightarrow$$
 Fe(CNS)<sub>3</sub> + 3Cl<sup>-</sup> ]

Blood red

- 21. When K<sub>2</sub>CrO<sub>4</sub> is added to CuSO<sub>4</sub> solution, there is formation of CuCrO<sub>4</sub> and CuCr<sub>2</sub>O<sub>7</sub>. Formation of CuCr<sub>2</sub>O<sub>7</sub> is due to :
  - (a) basic nature of CuSO<sub>4</sub> solution which converts CrO<sub>4</sub><sup>2-</sup> to Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>
  - (b) acidic nature of CuSO<sub>4</sub> solution which converts CrO<sub>4</sub><sup>2</sup> to  $Cr_2O_7^{2-}$
  - (c) CuSO<sub>4</sub> has a typical property of converting CrO<sub>4</sub><sup>2-</sup> to  $Cr_2O_7^2$
  - (d) none of the above is correct
- 22. More number of oxidation states are exhibited by the actinoids than by the lanthanoids. The main reason for this is:

[A.I.E.E.E. 2008]

- (a) greater metallic character of the lanthanides than that of the corresponding actinides
- (b) lesser energy difference between 5f and 6d-orbitals than that between 4f and 5d-orbitals
- (c) more active nature of actinoids
- (d) more energy difference between 5f and 6d-orbitals than that between 4f and 5d-orbitals
- 23. Among the following transition elements, pick out the element(s) with highest second ionisation energy:
  - (i) V(Z=23) (ii) Cr(Z=24) (iii) Mn(Z=25) (iv) Cu(Z=29)
  - (v) Zn(Z = 30)
  - (a) (i) and (iii)
- (b) (ii) and (iv)
- (c) (ii) and (v)
- (d) (iv) only

[Hint: Cu<sup>+</sup> has stable configuration, [Ar]3d<sup>10</sup>.]

#### tuswers 1. (b) 2. (c) 3. (d) 4. (a) 5. (b) 6. (c) 7. (a) 8. (d) 9. (a) **10.** (c) **11.** (b) 12. (d) 13. (b) 15. (d) 16. (d) **19.** (c) 14. (c) 17. (a) 18. (b) 20. (d) 21. (b) 22. (b) 23. (d)

## Matrix Matching Questions for IIT Aspirants

1.	Match the Column-I with	n Column-II:	7.	Match the ions of List-I with	h their characteristics in List-II:
	Column-I	Column-II		List-I	List-II
	(a) Tc (	p) Transition element		(a) $Fe^{3+}$	(p) White precipitate with NaCl
		q) Not found in nature		(b) Fe <sup>2+</sup>	(q) Blood red colour with KCNS
	· · ·	r) Last element of third transition series		(c) Cu <sup>2+</sup>	(r) Prussian blue
	• • • • • • • • • • • • • • • • • • • •	s) Used in galvanization of iron		(d) Ag <sup>+</sup>	(s) Turnbull's blue
2.	·	in List-I with their properties in			(t) Chocolate brown precipitate
	List-II:	r r r r r r r r r r r r r r r r r r r			with K <sub>4</sub> Fe(CN) <sub>6</sub>
	List-I	List-∏	8.	Match the element in List-I	with their properties in List-II:
	(a) K <sub>2</sub> MnO <sub>4</sub>	(p) Transition element in +6 state		List-I	List-II
	(b) $KMnO_4$	(q) Oxidising agent in acid medium		(a) Fe	(p) Do not form amalgam
	(c) $K_2Cr_2O_7$	(r) Manufactured from pyrolusite ore		(b) Pt	
	(d) $K_2CrO_4$	(s) Manufactured from chromite ore		(c) Mo	(r) Used in biological oxidation of
<b>3</b>	Match List-I with List-I	AND IN THE PERSON NAMED IN COLUMN TWO IS NOT THE PERSON NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO IS NAMED IN COLUMN TWO			H <sub>2</sub> O to O <sub>2</sub>
٠.				(d) Mn	(s) Used in X-ray tube
	List-I	List-II	9.	Match List-I with List-II:	(5) Coca in A lay tace
	(Property)	(Transition elements)		List-I	List-II
	(a) Highest oxidation stat	** ·			
	(b) Highest density	(q) Os		(a) Ni <sup>2+</sup>	(p) Alloy
	(c) Element with maximu	m (r) Tc		(b) Ti	(q) Diamagnetic character
	unpaired electrons	(a) B.		(c) Misch metal	(r) $3d^2$
4	(d) Radioactive transition	•	10	(d) Hg	(s) $\sqrt{8}$ B.M. (Magnetic moment)
4.	List-II:	st-I with their metal composition in	10.	Match List-I with List-II:	•
				List-I	List-II
	List-I	List-II		(a) Cu <sup>2+</sup>	(p) Form amphoteric oxide
	(a) German silver	(p) Cu		(b) $Zn^{2+}$	(q) Diamagnetic and colourless
	(b) Gun metal	(q) Zn	•		compounds
	(c) Brass	(r) Ni		(c) Cr <sup>3+</sup>	(r) Form complex with NH <sub>3</sub>
	(d) Solder	(s) Sn		(d) $Sc^{3+}$	(s) Form complex with KCN
_		(t) Pb	11.	Match Column-I with Colum	ın-II:
5.	Match List-I with List-I	I and List-III:		Column-I	Column-II
	List-I	List-III List-III		(a) Baeyer's reagent	(p) $CuSO_4 + Ca(OH)_2$
	(a) Reduction	(p) Adam's catalyst (u) TiCl <sub>4</sub>		(b) Equivalent mass = 158	(q) 1% alkaline KMnO <sub>4</sub>
	(b) Polythene production	(g) Wacker process (v) Pt		(c) Bordeaux mixture	(r) Detection of unsaturation
	(c) Aldehyde manufactur			•	in organic compounds
6.	Match List-I with List-I	I:		(d) Nessler's reagent	(s) Complex of mercury
	List-I	List-II			,
	(a) Ag <sup>+</sup> (Isoelectronic) w	rith (p) Diamagnetic		•	
	(b) $Zn^{2+}$	(q) Cd <sup>2+</sup>			
-	(c) Element with lowest				
	(d) Cr	(s) Paramagnetic			•
	. ,				
	A				
Ц	Answers —				
1.	(a-p, q) (b-p, r)	(c-p, s) (d-q)	7.	(a-q, r) $(b-s)$ $(c-t)$	(d-p)
2.	(a-p, r) (b-q, r)	(c-p, q, s) (d-p, s)	8.		(d-r)
3.	(a-q, s) $(b-q)$	(c-p) (d-r)	9.	(a-s) $(b-r, s)$ $(c-p)$	(d-q)
4	(a - a - a) (b - a - a)	() · (4 - 4)	10	(a - a) (b - a - a) (a - a	) (4)

**10.** (a-r, s)

11. (a-q, r)

(b-p, q, r)

(b-q)

(c-p, r, s)

(c-p)

(d-q)

(d-s)

(d-s, t)

(d-s)

(c-p, q)

(c-q-w)

(a-p, q, r) (b-p, q, s)

(b-r-u)

(b-p)

5. (a-p-v)

(a-p, q)

## **Assertion-Reason Type Questions**

Following questions consist of an Assertion (A) and Reason (R). Use the following key to choose the correct answer:

- (a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
- (c) If (A) is correct but (R) is incorrect.
- (d) If (A) is incorrect but (R) is correct.
- 1. (A) Tungsten has a very high melting point.
  - (R) Tungsten is a covalent compound. [A.I.I.M.S. 1997]
- 2. (A) Mn-atom loses ns electrons first during ionisation as compared to (n-1)d electrons.
  - (R) The effective nuclear charge experienced by (n-1)d electrons is greater than that by ns electrons.

[A.I.I.M.S. 2001]

- 3. (A) KMnO<sub>4</sub> is a coloured compound.
  - (R) Colour of KMnO<sub>4</sub> is due to charge transfer.
- 4. (A) TiCl<sub>4</sub> is a colourless compound.
  - (R) Ti<sup>4+</sup> ion has no unpaired electron.
- (A) KMnO<sub>4</sub> is oxidising agent in neutral, acidic and in basic medium.
  - (R) Equivalent mass of KMnO<sub>4</sub> in acidic medium is 31.6.

- **6.** (A)  $K_2CrO_4$  is yellow coloured compound.
  - (R) Chromate ion has tetrahedral geometry.
- 7. (A) Solution of Na<sub>2</sub>CrO<sub>4</sub> in water is intensely coloured.
  - (R) Oxidation state of Cr in Na<sub>2</sub>CrO<sub>4</sub> is (+VI).

[A.I.I.M.S. 2003]

- **8.** (A) All the members of actinide series are radioactive in nature.
  - (R) The electrons are gradually accommodated in 5f-energy subshell.
- 9. (A) The spin only magnetic moment of  $Sc^{3+}$  is 1.73 B.M.
  - (R) The spin only magnetic moment of an ion is equal to  $\sqrt{n(n+2)}$ ; where *n* is the number of unpaired electrons in the ion.
- **10.** (A) Potassium ferrocyanide is diamagnetic whereas potassium ferricyanide is paramagnetic.
  - (R) Crystal field splitting in ferrocyanide ion is greater than that of ferricyanide ion.
- 11. (A) The free gaseous Cr-atom has six unpaired electrons.
  - (R) Half filled s-orbital has greater stability.
- 12. (A) Ionisation of transition metals involve loss of ns electrons before (n-1)d electrons.
  - (R) Filling of *ns*-orbitals take place before the filling of (n-1)d-orbitals.

## Answers

1. (c)

2. (a)

**3.** (a)

**4.** (a)

**5.** (b)

**6.** (b)

. 7. (b)

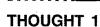
8. (b)

9. (d)

10. (c)

11. (c) 12. (b)

## THOUGHT TYPE QUESTIONS



Two types of magnetic behaviour are found in substances:
(a) Diamagnetism and (b) Paramagnetism

Diamagnetic substances are those which are repelled by an applied magnetic field. Such substances have no unpaired electron. Paramagnetic substances are those which are attracted by an applied magnetic field. Transition metals and many of their compounds show paramagnetic behaviour where there are unpaired electron or electrons. The magnetic moment arise from the spin and orbital motions in ions or molecules. Magnetic moment of n unpaired electrons is given as,

$$\mu = \sqrt{n(n+2)}$$
 Bohr Magneton

Magnetic moment increases as the number of unpaired electrons increases.

- 1. In 3d series, the maximum magnetic moment is shown by:
  - (a) Sc (At. no. 21)

(b) V(23)

(c) Cr (24)

(d) Fe (26)

[Hint: Cr-atom has maximum number of unpaired electrons, i.e., 6. Hence, the magnetic moment =  $\sqrt{6 \times 8} = \sqrt{48}$  B.M.]

2. Which among the following ions has maximum value of magnetic moment?

(a)  $Cu^{2+}$ 

(b) Mn<sup>24</sup>

(c) Cr<sup>2+</sup>

(d)  $Ti^{24}$ 

[Hint: 
$$Cu^{2+}$$
 E.C. = 2, 8, 8 + 9,  $\mu = \sqrt{3}$  B.M.; 
$$Mn^{2+}$$
 E.C. = 2, 8, 8 + 5,  $\mu = \sqrt{35}$  B.M.; 
$$Cr^{2+}$$
 E.C. = 2, 8, 8 + 4,  $\mu = \sqrt{24}$  B.M.; 
$$Ti^{2+}$$
 E.C. = 2, 8, 8 + 2,  $\mu = \sqrt{8}$  B.M.]

3. Increasing value of magnetic moments of (I)  $[Fe(CN)_6]^{4-}$ , (II)  $[Fe(CN)_6]^{3-}$ , (III)  $[Cr(NH_3)_6]^{3+}$ , (IV)  $[Ni(H_2O)_4]^{2+}$  is:

- (a) I < II < III < IV
- (b) IV < III < II < I
- (c) II < III < I < IV
- (d) I < II < IV < III

[Hint:  $[Fe(CN)_6]^4$  unpaired electron = 0;  $[Fe(CN)_6]^{3-}$  unpaired electron = 1;  $[Cr(NH_3)_6]^{3+}$  unpaired electron = 3;

 $[Ni(H_2O)_4]^{2+}$  unpaired electron = 2]

- 4. Magnetic moment of [Ni(CN)<sub>4</sub>]<sup>2-</sup> is zero but that of  $[Ni(H_2O)_4]^{2+}$  is 2.83 B.M. It is because of:
  - (a) CN is a strong ligand making two unpaired electrons in  $Ni^{2+}$  to pair up, while in  $[Ni(H_2O)_4]^{2+}$  two electrons remain unpaired as H2O is a weak ligand
  - (b) different oxidation state of Ni in two complexes
  - (c) both (a) and (b)
  - (d) none of the above
- 5. Magnetic moments of Cr (Z = 24), Mn<sup>+</sup> (Z = 25) and Fe<sup>2+</sup> (Z = 26) are x, y and z respectively. Which of the following order is correct?
  - (a) x < y < z
- (b) x = y < z
- (c) z < x = y
- (d) x = y = z

**Hint**:  $x = \sqrt{48}$ ;  $y = \sqrt{48}$ ;  $z = \sqrt{24}$ 

Cr = 6 unpaired electrons,  $Mn^+ = 6$  unpaired electrons.  $Fe^{2+} = 4$  unpaired electrons.

- 6. There are three unpaired electrons in  $[Co(H_2O)_6]^{2+}$  and calculated value of magnetic moment on the basis of  $\sqrt{n(n+2)}$  formula is 3.87 B.M. which is lower than the experimental value of 4.40 B.M. The reason for this difference is due to:
  - (a) increase in number of unpaired electrons during determination
  - (b) some contribution of the orbital motion of the electrons to the magnetic moment
  - (c) d-d transition
  - (d) experimental error

## THOUGHT 2

Most of the compounds of the transition metals are coloured in the solid or in solution states. The colour of the transition metal ions arises from the excitation of electrons from the d-orbitals of lower energy to the d-orbitals of higher energy. The energy required for d-d electron excitation is available in the visible range. Transition metal ions have the tendency to absorb certain radiations from the visible region and exhibit the complementary colour.

The transition metal ions which have completely filled d-orbitals are colourless as the excitation of electron or electrons is not possible within d-orbitals. The transition metal ions which have completely empty d-orbitals are also colourless. In certain oxysalts of transition elements like KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, there are no unpaired electrons at the central atom but they are deep in colour. The colour of these compounds is due to charge transfer spectrum. For example, in MnO<sub>4</sub>, an electron is momentarily transferred from O to the metal and thus oxygen changes from  $O^{2-}$  to  $O^{-}$  and manganese from Mn(+VII) to Mn(+VI).

- 1. Select the correct statement:
  - (a) Colour of the transition metal ion arises due to d-d transition
  - (b) Colour of certain oxysalts of transition metals is due to charge transfer
  - (c) Both are correct
  - (d) None is correct
- Which of the following is paramagnetic as well as coloured ion?
  - (a) Cu<sup>+</sup>

(b) Cu<sup>2+</sup>

(c)  $Sc^{3+}$ 

- (d)  $Zn^{2+}$
- **3.** Which is a coloured ion?
  - (a)  $[Cr(H_2O)_6]^{3+}$
- (c)  $[Ti(H_2O)_6]^{4+}$
- (b) [Cu(CN)<sub>4</sub>]<sup>3-</sup> (d) [Sc(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>
- 4. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> gives coloured solution in water. The colour is due
  - (a) d-d transition in Cr-atoms
  - (b) presence of unpaired electron in d-orbital in oxygen
  - (c) charge transfer from O to Cr
  - (d) none of the above
- 5. Which of the following compounds is (are) coloured due to charge transfer spectra and not due to d-d transitions?
  - (a) KMnO<sub>4</sub>
- (b) K2CrO4

(c) CrO<sub>3</sub>

(d) all of these

## THOUGHT 3

Photography is based on the nature of silver halides. Except AgF, the silver halides are photosensitive. These undergo decomposition in light and turn black due to formation of free silver.

$$2AgBr \xrightarrow{Light} 2Ag + Br_2$$

The photographic plates or films are prepared in a dark and dustfree room by applying a light sensitive mixture called emulsion which is prepared by adding 20 per cent aqueous solution of silver nitrate to ammonium bromide solution containing gelatin.

When such a film is exposed, the emulsion gets affected. Since different parts of the body reflect light of varied intensity, the film or plate is affected proportionately. An actual but inverted image of the object is thus formed on the film or plate which is not visible to the eye. It is, therefore, called the latent image.

When this exposed film or plate is dipped in a developer which contains a reducing agent, the parts affected most during exposure are reduced to the maximum. The image becomes visible. It is called a negative. The remaining sensitive emulsion on the negative is removed by dissolving it in hypo solution (fixer). Finally, a positive of the negative already prepared is made on silver bromide paper.

- The compound formed on the unexposed photographic film or plate is:
  - (a) silver nitrate
- (b) ammonium bromide
- (c) diamminesilver bromide (d) silver bromide
- The exposed part of the film or plate after developing contains:

- (a) silver metal
- (b) silver oxide
- (c) silver bromide
- (d) silver nitrate
- 3. The solution of the developer consists:
  - (a) alkaline solution of pyrogallol
  - (b) alkaline solution of quinol
  - (c) either (a) or (b)
  - (d) neither (a) nor (b)
- 4. Silver halides are used in photography because these compounds:
  - (a) are insoluble in water
- (b) are affected by light
- (c) are soluble in ammonia solution
- (d) easily stick on the surface of photographic plate or film
- 5. Silver bromide dissolves in hypo solution forming:
  - (a)  $Ag_2S_2O_3$
- (b) Ag<sub>2</sub>S
- (c)  $Na_3[Ag(S_2O_3)_2]$
- (d) NaAgS<sub>2</sub>O<sub>3</sub>

#### THOUGHT 4

The process of corrosion of iron is known as rusting. Rust appears to be a hydrated ferric oxide, Fe<sub>2</sub>O<sub>3</sub>·xH<sub>2</sub>O. Both O<sub>2</sub> and H<sub>2</sub>O are required for rusting. Iron can be protected from the rusting by use of following methods:

- (i) Applying paints, lacquers and enamels on the surface of iron.
- (ii) By forming a firm and coherent protective coating of ferrosoferric oxide. This is done by passing steam over hot iron.
- (iii) By coating a thin film of zinc, tin, nickel, chromium, aluminium, etc., on the surface of iron.

If plated with zinc, the reaction products of zinc with O2 and H<sub>2</sub>O form a coating which sticks to the surface and thereby protects iron.

- 1. Rusting is a corrosion process in which:
  - (a) Zn reacts with O2
  - (b) Sn reacts with O2 and H2O
  - (c) Fe is converted into hydrated ferric oxide
  - (d) minute holes are formed on the surface of a metal
- Zinc protects iron from corrosion because:
  - (a) it is an active metal
  - (b) a sticky coating is formed on its surface on exposure to
  - (c) it is not affected by atmosphere
  - (d) it has lower oxidation potential than iron

- 3. Galvanisation means:
  - (a) deposition of Zn on Fe
  - (b) deposition of Al on Fe
  - (c) deposition of Sn on Fe
  - (d), deposition of Cu on Fe
- 4. Corrosion is an electrochemical process. It involves:
  - (a) loss of electrons by iron, Fe  $\longrightarrow$  Fe<sup>2+</sup> + 2e, i.e., iron acts as an anode.
  - (b) impurities act as a cathode. Electrons are used in forming hydroxyl ions.

$$H_2O + O + 2e \longrightarrow 2OH$$

(c) ferrous ions are oxidised to ferric ions in presence of dissolved oxygen.

$$2Fe^{2+} + O + H_2O \longrightarrow 2Fe^{3+} + 2OH^{-}$$

- (d) all the above reactions
- 5. For prevention of rusting of iron, which is used in paints?
  - (a) PbO

- (b) PbO<sub>2</sub>
- (c) Pb<sub>3</sub>O<sub>4</sub>
- (d) PbSO<sub>4</sub>

#### **THOUGHT 5**

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite (CuSO<sub>4</sub>·5H<sub>2</sub>O), atacamite [Cu<sub>2</sub>Cl(OH)<sub>3</sub>], Cuprite (Cu2O), copper glance (Cu2S) and malachite [Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>]. However, 80% of the world's copper production comes from the ore chalcopyrite (CuFeS2). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and [I.I.T. 2010] self reduction.

- 1. Partial roasting of chalcopyrite produces:
  - (a) Cu<sub>2</sub>S and FeO
- (b) Cu<sub>2</sub>O and FeO
- (c) CuS and Fe<sub>2</sub>O<sub>3</sub>
- (d) Cu<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub>
- 2. Iron is removed from chalcopyrite as:
  - (a) FeO

- (b) FeS
- (c) Fe<sub>2</sub>O<sub>3</sub>
- (d) FeSiO<sub>3</sub>
- 3. In self reduction, the reducing species is:

(b)  $O^{2-}$ 

(c)  $S^{2-}$ 

(d)  $SO_2$ 

Thought 1 Thought 4 1, (c) 2. (b) 3. (d) **4.** (a) 5. (c) **6.** (b) 5. (c) **1.** (c) **2.** (b) 3. (a) **4.** (d) Thought 2 1. (c) 2. (b) 3. (a) **4.** (c) 5. (d) Thought 5 1. (b) 2. (d) 3. (c)

Thought 3 1. (d) 2. (a) 3. (c) **4.** (b) 5. (c)

#### BRAIN STORMING PROBLEMS

1. Explain, why Mn<sup>3+</sup> is less stable than Mn<sup>2+</sup> and Mn<sup>4+</sup> ions?

Explain, why Mn<sup>3+</sup> disproportionate into Mn<sup>2+</sup> and Mn<sup>4+</sup>

 $Mn^{3+} \longrightarrow 3d^4, 4s^0$   $Mn^{4+} \longrightarrow 3d^3, 4s^0$ [Ans.  $Mn_{25} \longrightarrow 3d^5, 4s^2;$   $Mn^{2+} \longrightarrow 3d^5, 4s^0;$ 

On the basis of electronic configuration, Mn<sup>2+</sup> and Mn<sup>4+</sup> are expected to be more stable, hence, Mn<sup>3+</sup> undergoes disproportionation.

 $2Mn^{3+} \longrightarrow Mn^{2+} + Mn^{4+}$ 

2. Standard reduction potential of copper is greater than that of hydrogen vet it liberates hydrogen from a concentrated solution of hydrochloric acid. Explain this fact with proper reasoning.

 $Cu^{2+} + 2e \longrightarrow Cu(s)$ ;  $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ volt}$  $2H^{+}+2e\longrightarrow H_{2}(g)$ ;  $E^{\circ}_{H^{+}/H_{2}} = 0.00 \text{ volt}$ 

[Ans. When copper is treated with conc. HCl then formation of stable complex ion [CuCl<sub>4</sub>]<sup>2-</sup> along with liberation of H<sub>2</sub> gas takes place.

 $Cu + 4HCl(conc.) \longrightarrow [CuCl_4]^{2-} + 2H^+ + H_2^{\uparrow}$ 

- 3. Account for the following facts:
  - (a) An aqueous solution of FeCl<sub>3</sub> is slightly yellowish in
  - (b) Cu(I) compounds are not known in aqueous solution. [Ans.
    - (a) An aqueous solution of FeCl<sub>3</sub> is colloidal. It is yellowish in colour due to Tyndall effect.
    - (b) Cu(I) compounds undergo disproportionation in aqueous medium.

$$Cu_2Cl_2 \longrightarrow CuCl_2 + Cu]$$

- 4. Answer the following questions:
  - (a) Which is more basic?

(i) ZrO<sub>2</sub> or TiO<sub>2</sub>

(ii)  $V_2O_5$  or  $Nb_2O_5$ 

(iii) OsO<sub>4</sub> or ReO<sub>2</sub>

- (b) Which is more stable  $[CoCl_6]^{3-}$  or  $[IrCl_6]^{3-}$ ?
- (c) Which forms trans isomer [PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] or.  $[PtCl(NH_3)_3]^{\dagger}$ ?
- (d) Which is more oxidising agent Cr(VI) or Mo(VI)? Ans.
  - (a) (i) ZrO<sub>2</sub> (ii) Nb<sub>2</sub>O<sub>5</sub> (iii) ReO<sub>2</sub>
  - (b)  $[IrCl_6]^{3-}$  is more stable than  $[CoCl_6]^{3-}$  because in +3 state Ir is more stable than Co.
  - (c) [PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] will form trans isomer.
  - (d) Cr(VI) is stronger oxidising agent than Mo(VI).]
- 5. Write down the names of crystal structures in which the following elements are present.

Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

[Ans.	Element	Crystal Structure
	Sc	fcc
	Ti	hcp
	V	bcc
	Cr	bcc
	Mn	bcc, tet

Fe	bcc, fcc
· Co	fcc, hcp
Ni	fcc
Cu	fcc
Zn	hcp ]

- **6.** Write down the name of catalyst for the following:
  - (i) In the synthesis of hydrocarbon in Fischer-Tropsch process.
  - (ii) Adams catalyst in reduction.
  - (iii) Deacon's process of making Cl<sub>2</sub> from HCl.
  - (iv) Reppe synthesis of benzene.
  - (v) Fenton's reagent in the synthesis of aldehydes from alcohols.

[Ans. (i) Co/Fe (ii) Pt/PtO (iii) CuCl<sub>2</sub> (iv) Ni complexes (v) FeSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> ---

7. (a) Calculate magnetic moment of  $Fe^{3+}$  in  $[Fe(CN)_6]^{3-}$  and in  $[Fe(H_2O)_6]^{3+}$ .

> [Hint: In [Fe(CN)<sub>6</sub>]<sup>3-</sup>, Fe<sup>3+</sup> ion has only one unpaired electron. Thus, magnetic moment of Fe<sup>3+</sup> will be  $\sqrt{3}$ , i.e., 1.732 B.M.  $(\mu_p = \sqrt{n(n+2)})$  B.M., where, n. is number of unpaired electrons). In [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, Fe<sup>3+</sup> ion has 5 unpaired electrons, hence, its magnetic moment will be  $\sqrt{35}$  B.M., i.e., 5.92 B.M.]

(b) Arrange following complexes in decreasing order of magnetic moment:

 $[Ni(H_2O)_4]^{2+}$ ,  $[Ni(CN)_4]^{2-}$ ,  $[Fe(CN)_6]^{3-}$ ,  $[Fe(CN)_6]^{4-}$ 

 $[Fe(CN)_6]^{4-} = [Ni(CN)_4]^{2-} < [Fe(CN)_6]^{3-} <$  $[Ni(H_2O)_4]^{2+}]$ 

[Hint: In  $[Fe(CN)_6]^4$  and  $[Ni(CN)_4]^{2-}$ , central atom has no unpaired electron, hence, their magnetic moment is zero. In  $[\text{Fe}(\text{CN})_6]^{3-}$ , there is only one electron with central Fe<sup>3+</sup> ion, hence, its magnetic moment will be 1.732 B.M. In  $[Ni(H_2O)_4]^{2+}$ , there are two unpaired electrons with Ni<sup>2+</sup> and hence, its magnetic moment will be  $\sqrt{8}$  B.M.]

8. Give the formula of three ions which are coloured due to charge transfer spectra.

[Ans.  $VO_2^+$ ,  $CrO_4^{2-}$ ,  $MnO_4^-$ ]

[Hint: Oxidation state of Ion Colour central atom  $VO_2^+$ +5 pale yellow  $CrO_4^{2-}$ +6 dark yellow  $MnO_4$ +7 dark purple

- 9. What happens when?
  - (i) CO<sub>2</sub> gas is passed through aqueous solution of Na<sub>2</sub>CrO<sub>4</sub>.
  - (ii) Ammonium dichromate is heated strongly.
  - (iii) Two gases 'A' and 'B' turns acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> green. When these gases are passed through water simultaneously, solution turns turbid yellow. What are the gases 'A' and 'B'?

[Ans. (i) Sodium dichromate, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is formed,

(ii) N<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> are formed,

(iii) 'A' and 'B' are SO<sub>2</sub> and H<sub>2</sub>S.]

 $\textbf{[Hint: (i) } H_2O + CO_2 \longrightarrow H_2CO_3$ 

Carbonic acid

 $2Na_2CrO_4 + H_2CO_3 \longrightarrow Na_2CO_3 + Na_2Cr_2O_7 + H_2O_3$ 

(ii) 
$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$$

(iii) 
$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$\{H_2S + [O] \longrightarrow H_2O + S\} \times 3$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$
Green

When both SO<sub>2</sub> and H<sub>2</sub>S are passed simultaneously through water then colloidal sulphur is precipitated.

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$
 ]

Yellowish turbidity

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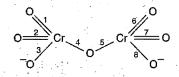
The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. How many number of unpaired electrons are present in  $Mn^{2+}$ ?
- 2. What is the magnetic moment of Fe<sup>3+</sup>?
- 3. How many sigma bonds are present in  $Cr_2O_7^{2-}$  ion?
- **4.** How many electrons are involved in the reduction of KMnO<sub>4</sub> in acidic medium?
- 5. The change in the oxidation number of chromium in potassium dichromate when it acts as an oxidising agent is:
- **6.** How many water molecules are associated with a molecule of Mohr's salt?
- 7. When ammonium hydroxide is added to copper sulphate, a blue coloured complex is formed. What is the coordination number of copper in the complex?
- 8. The percentage of impurity in the 23 carat gold is:

### Answers

1. (5) The at. no. of Mn is 25. The number of electrons associated with  $Mn^{2+} = 23$ 

- 2. (6) The electronic configuration of Fe<sup>3+</sup> is : 2, 8, 8 +5. Mag. moment =  $\sqrt{5 \times 7} \approx 6$
- 3. (8) The structure of dichromate ion is



- 4. (5)  $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
- 5. (3)  $\operatorname{Cr}_2\operatorname{O}_7^{2-} \longrightarrow 2\operatorname{Cr}^{3+}$

Oxidation number of Cr in  $Cr_2O_7^{2-}$  is +6, change (6-3)=3

- 6. (6) The formula of Mohr's salt is: FeSO<sub>4</sub> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 6H<sub>2</sub>O
- 7. (4) The blue complex is, [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>.
- **8.** (4) % Gold =  $\frac{100}{24} \times 23 = 96$

Impurities percentage (100 - 96) = 4

## CHAPTER 15

# Coordination Compounds and Organometallics

#### Contents:

- 15.1 Molecular or Addition Compounds
- 15.2 Terminology of Coordination Compounds
- 15.3 Nomenclature of Coordination Compounds
- 15.4 Werner's Coordination Theory
- 15.5 Isomerism in Coordination Compounds
- 15.6 Bonding in Coordination Compounds:
  - (1) Valence Bond Theory
  - (2) Crystal Field Theory
- 15.7 Stability of Coordination Compounds in Solutions
- 15.8 Preparation of Coordination Compounds
- 15.9 Importance of Coordination Compounds
- 15.10 Organometallic Compounds

One of the most important properties of transition metals is that they form coordination or complex compounds. These compounds play a vital role in our lives. The importance of these compounds can be realised from the fact that life would not have been possible without the existence of **chlorophyll** (Mg-complex) in plants and haemoglobin (Fe-complex) in the blood of animals. One of the earliest known coordination compound is prussian blue which was accidently prepared in 1704 by a Berlin colour maker, **Diesbach**, by strongly heating animal wastes and sodium carbonate in an iron container. In 1753, Macquer prepared potassium ferrocyanide by treating prussian blue with alkali. In 1799, Tassaert obtained an orange compound, CoCl<sub>3</sub>·6NH<sub>3</sub>, by allowing a mixture of cobalt chloride and aqueous ammonia to stand in air. During the next fifty years, numerous compounds of this type containing cobalt, platinum, chromium and iron were discovered. The field of such compounds has expanded very fast in recent years and coordination compounds are playing important roles in analytical chemistry, polymerization reactions, metallurgy and refining of metals, organic synthesis, electroplating, photography, biochemistry, water purification, textile dyeing and bacteriology. In addition, the study of these compounds has enlarged our understanding of chemical bonding, certain physical properties such as spectral and magnetic properties and metabolic processes. In this chapter some basic aspects regarding coordination compounds are discussed.

#### 15.1 MOLECULAR OR ADDITION COMPOUNDS

When solutions containing two or more simple stable compounds in molecular proportions are allowed to evaporate, crystals of new substances are obtained. These substances are termed **molecular** or **addition compounds**. Some common examples are:

$$\begin{split} KCl + MgCl_2 + 6H_2O &\longrightarrow KCl \cdot MgCl_2 \cdot 6H_2O \\ &\quad Carnallite \\ K_2SO_4 + Al_2(SO_4)_3 + 24H_2O &\longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \\ &\quad Alum \\ FeSO_4 + (NH_4)_2SO_4 + 6H_2O &\longrightarrow FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \\ &\quad Mohr's \ salt \\ 4KCN + Fe(CN)_2 &\longrightarrow Fe(CN)_2 \cdot 4KCN \end{split}$$

$$\begin{array}{c} \text{CuSO}_4 \,+\, 4\text{NH}_3 \longrightarrow \text{CuSO}_4{\cdot}4\text{NH}_3 \\ \text{AgCN} \,+\, \text{KCN} \longrightarrow \text{KCN-AgCN} \\ \text{Simple stable} & \text{Addition or molecular} \\ \text{compounds} & \text{compounds} \end{array}$$

The molecular or addition compounds are of two types:

(i) **Double salts or Lattice compounds:** The addition compounds which are stable in solid state only but are broken down into individual constituents when dissolved in water are called **double salts** or **lattice compounds.** Their solutions have the same properties as the mixture of individual compounds. For example, when Mohr's salt, [FeSO<sub>4</sub>·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O], is dissolved in water, it exhibits the properties of FeSO<sub>4</sub> and  $(NH_4)_2SO_4$ , *i.e.*, they produce Fe<sup>2+</sup>,  $NH_4$ <sup>+</sup> and  $SO_4$ <sup>2-</sup> ions in solution. Thus, each ion has its identity in double salt.

$$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \longrightarrow Fe^{2+}(aq.) + 2NH_4^+(aq.)$$

$$Mohr's salt \longrightarrow +2SO_4^{2-}(aq.) + 6H_2O$$

Carnallite, KCl-MgCl<sub>2</sub>·6H<sub>2</sub>O; potash alum,

K<sub>2</sub>SO<sub>4</sub>·Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O,etc., are the examples of double salts.

(ii) Coordination or complex compounds: The addition compounds in which some of the constituent ions or molecules lose their identity and when dissolved in water they do not break up completely into individual ions, are called **coordination compounds.** The properties of their solutions are different than those of their constituents. When crystals of  $CuSO_4$ ·4NH<sub>3</sub> are dissolved in water there is hardly any evidence for the presence of  $Cu^{2+}$ ions or ammonia molecules. A new ion,  $[Cu(NH_3)_4]^{2+}$ , is furnished in which ammonia molecules are directly linked with the metal ion. Similarly, the aqueous solution of  $Fe(CN)_2$ ·4KCN does not give tests of  $Fe^{2+}$  and  $CN^-$  ions but gives the test for a new ion,  $[Fe(CN)_6]^{4-}$ . The ions  $[Cu(NH_3)_4]^{2+}$  and  $[Fe(CN)_6]^{4-}$  are called **complex ions**.

$$\text{CuSO}_4 \cdot 4\text{NH}_3 \Longrightarrow \left[\text{Cu(NH}_3)_4\right]^{2+} + \text{SO}_4^{2-}$$
  
 $\text{Fe(CN)}_2 \cdot 4\text{KCN} \Longrightarrow 4\text{K}^+ + \left[\text{Fe(CN)}_6\right]^{4-}$ 

Thus, a coordination or complex compound may be defined as a molecular compound that results from the combination of two or more simple stable molecular compounds and retains its identity in the solid as well as in dissolved state. The properties of such compounds are totally different than individual constituents. A coordination compound contains very often but not always a complex ion.

Some of the common examples of these compounds are:

A complex ion may be defined as an electrically charged radical which consists of a central metal atom or ion

surrounded by a group of ions or neutral molecules or both. A coordination compound, thus, consists of either,

- (i) a simple cation and a complex anion such as  $K_4[Fe(CN)_6]$ , or
- (ii) a complex cation and a simple anion such as [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>, or
- (iii) a complex cation and a complex anion such as  $[Co(NH_3)_6][Cr(C_2O_4)_3]$ , or
- (iv) a neutral molecule such as Cu(Gly)<sub>2</sub>, Ni(CO)<sub>4</sub>, Ni(DMG)<sub>2</sub>, etc.

## 15.2 TERMINOLOGY OF COORDINATION COMPOUNDS

Before further discussion, it is necessary to explain some important terms used in the study of coordination compounds. These are discussed here.

#### 3 1. Ligands

The neutral molecules; anions or cations which are directly linked with the central metal atom or ion in a complex ion are called **ligands**. The ligands are attached to the central metal ion or atom through coordinate bonds or dative linkage. With few exceptions, free ligands have at least one electron pair that is not engaged in bonding. Some examples are:

$$H-\ddot{N}-H$$
  $H-\ddot{O}$ :  $C\equiv \bar{N}$ :

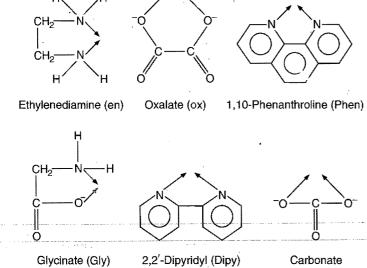
The ligand acts as a donor as it donates one or more electron pairs to the central metal atom or ion which acts as an acceptor. The ligands are thus Lewis bases and central metal ions or atoms are Lewis acids. The formation of a complex ion involves following two things:

- (i) Ligands should have lone pair or pairs of electrons which can be donated to the central metal ion or atom.
- (ii) The central atom or ion should have vacant orbitals of nearly equivalent energy as to accommodate the electrons donated by ligands. This condition is easily fulfilled by atoms or ions of transition metals.

#### Types of ligands

Ligands can be of following types depending on the number of donor atoms present in them.

- (i) Mono- or unidentate ligands: They have one donor atom, *i.e.*, they supply only one electron pair to central metal atom or ion. F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, H<sub>2</sub>O, NH<sub>3</sub>, CN<sup>-</sup>, NO<sub>2</sub>, OH<sup>-</sup>, CO, etc., are examples of monodentate ligands.
- (ii) Bidentate ligands: Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands. Some examples are:

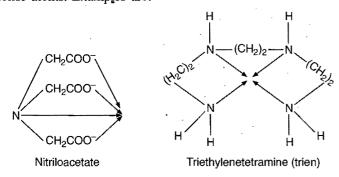


(iii) Tridentate ligands: The ligands having three donor atoms are called tridentate ligands. Examples are:

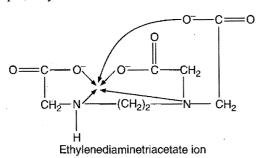
$$\begin{array}{c|c} H & H \\ H_2C & CH_2 \\ H_2C & N & CH_2 \\ \end{array}$$

$$\begin{array}{c|c} Diethylenetriamine (dien) & 2,2',2''-Terpyridine (terpy) \end{array}$$

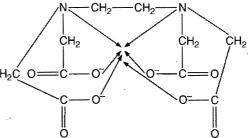
(iv) Tetradentate ligands: These ligands possess four donor atoms. Examples are:



(v) **Pentadentate ligands:** They have five donor atoms. For example, ethylenediaminetriacetate ion.



(vi) Hexadentate ligands: They have six donor atoms. The most important example is ethylenediaminetetraacetate ion



Ethylenediaminetetraacetate ion (EDTA)

(vii) Chelating ligands: A bidentate or a polydentate ligand is known as a chelating ligand if on coordination it results in the formation of a closed or cyclic ring structure. The complexes, thus formed are called chelates. The word chelate has been derived from the Greek word chele meaning claw. The complex formed by Cu<sup>2+</sup> ion with ethylenediamine is an example of a chelate.

$$\begin{bmatrix} \text{CH}_2 - \text{H}_2 \text{N} & \text{NH}_2 - \text{CH}_2 \\ \text{CH}_2 - \text{H}_2 \text{N} & \text{NH}_2 - \text{CH}_2 \end{bmatrix}^{2+} \\ \text{CH}_2 - \text{Cu}(\text{en})_2]^{2+} \end{bmatrix}$$

The following are the characteristics of chelates:

- (a) Chelating ligands form more stable complexes than monodentate ligands. This is called chelating effect. All types of polydentate ligands can act as **chelating ligands**.
- (b) The chelates containing 5 or 6-membered rings including metal atom are comparatively more stable. Chelating ligands which do not contain unsaturated groups (double bonds), in general, form five membered stable complexes while chelating ligands having unsaturated groups (double bonds) form sixmembered stable complexes.
- (c) Ligands with larger groups form more unstable rings than with smaller groups due to steric hindrance.

#### Importance of chelates

Chelates find wide applications in laboratory and industry:

- (i) A number of ions such as Cu<sup>2+</sup>, Ni<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, etc., are detected and estimated by the formation of stable and coloured chelates.
- (ii) In water softening.
- (iii) In separation of lanthanides and actinides.
- (iv) In the elimination of harmful radioactive metals from body. For this purpose usually EDTA is used.
- (v) In solvent extraction.
- (vi) In food preservation.

Name	Formula	Abbreviation	Dentate character
Carbonate	CO <sub>3</sub> <sup>2</sup> -		bidentate
Oxalate	$C_2O_4^{2-}$	ох	bidentate
Ethan-1,2-diamine	$NH_2$ — $CH_2$ — $CH_2$ — $NH_2$	en	bidentate
1,2-propanediamine	NH <sub>2</sub> —CH—CH <sub>2</sub> —NH <sub>2</sub>	pn	bidentate
	CH <sub>3</sub>		
	O O		
Acetylacetonato	$CH_3$ — $C$ = $CH$ — $C$ — $CH_3$	acac	bidentate
2,2'-dipyridine		bipy	bidentate
Glycinate	NH <sub>2</sub> —CH <sub>2</sub> —COO	gly	bidentate
Diethylenetriamine	NH(C <sub>2</sub> H <sub>4</sub> NH <sub>2</sub> ) <sub>2</sub>	dien	tridentate
	OOC—CH <sub>2</sub> CH <sub>2</sub> —COO	,	
Ethylenediaminetetraacetate	$N$ —CH <sub>2</sub> —CH <sub>2</sub> —N $\langle$	edta	hexadentate
•	-OOC—CH <sub>2</sub> CH <sub>2</sub> —COO-		× ×

#### SOME COMMON POLYDENTATE LIGANDS

- Note: (i) The ligands having two or more donor atoms are also called polydentate or multidentate ligands.
  - (ii) A multidentate ligand is known as a chelating ligand if on coordination it results in formation of a closed or cyclic ring. The complexes thus formed are called *Chelates*. The chelates are comparatively more stable than ordinary complexes.
  - (iii) Polydentate ligands have flexidentate character. It is not necessary that all the donor atoms present in the polydentate ligands should form coordinate bonds with central metal atom or ion. For example, ethylenediamine tetraacetic acid (EDTA) which is hexadentate ligand can function as pentadentate or tetradentate ligand with certain metal ions. Similarly sulphate ion can also act as monodentate ligand.
  - (iv) There are certain ligands which have two or more donor atoms but in forming complexes only one donor atom is attached to metal ion. Such ligands are called ambidentate ligands. Some examples of such ligands are:

$$\begin{array}{cccc} M \longleftarrow NO_2 & M \longleftarrow ONO \\ & Nitro & Nitrito \\ M \longleftarrow CN & M \longleftarrow NC \\ & Cyano & Isocyano \\ M \longleftarrow SCN & M \longleftarrow NCS \\ & Thiocyanide & Isothiocyanide \\ \end{array}$$

#### 2. Coordination number

The number of atoms of the ligands that are directly bound to the central metal atom or ion by coordinate bonds is known as the coordination number of the metal atom or ion. It is actually the number of chemical bonds which the ligands form with the central metal atom or ion. For example, in  $[Cu(NH_3)_4]^{2+}$  the coordination number of copper is 4, in  $[Co(en)_3]^{3+}$  the coordination number of cobalt is 6 as (en) is the bidentate

ligand. The most common coordination numbers exhibited by metal ions are 2, 4 and 6. The light transition metals exhibit 4 and 6 coordination numbers while heavy transition metals may exhibit coordination number more than 6. It has been observed that in a particular oxidation state, a metal prefers to exhibit the same coordination number.

C.N. =  $\Sigma$  Number of ligands  $\times$  Dentate character of ligands

Complex	Coordination number of central metal
$K_4[Fe(CN)_6]$	. 6
$[Ag(CN)_2]^-$	2
$[Pt(NH_3)_2Cl_2]$	4 .
$[Ca(edta)]^{2-}$	6
(edta is a hexadentate ligand)	

## 3. Coordination sphere or Coordination entity and counter ions

The central metal atom or ion and the ligands that are directly attached to it are enclosed in a square bracket. This has been called coordination sphere or first sphere of attraction or coordination entity. It behaves as a single unit because the ligands present in the coordination sphere are held tightly by the metal ion. Any ion present outside this sphere is separated from the complex when the compound is dissolved in the water, or any other polar medium. The ionizable groups written outside the bracket are called counter ions.

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$
  
 $[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^{-1}$ 

The charge on the complex ion is the algebraic sum of the charges carried by central metal ion and the ligands attached to it.

Charge on the complex ion = Oxidation number of metal ion + charge on the ligands

For illustration, see following examples:

**Example 1.** Assign the charge on the following ions: (a)  $[Hg(CN)_4]^x$ , (b)  $[Co(NH_3)_2Cl_4]^x$ , (c)  $[Fe(CN)_6]^x$ . Solution.

(a) The oxidation state of Hg in the complex is +2; So

$$x = +2 + 4 \times (-1) = -2$$
, i.e.,  $[Hg(CN)_4]^{2-}$ 

(b) The oxidation state of Co in the complex is +3; So

$$x = +3 + 2 \times 0 + 4 \times (-1)$$
  
= -1, *i.e.*, [Co(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>]

(c) The oxidation state of Fe in the complex is + 2; So

$$x = +2 + 6 \times (-1)$$
  
= -4, *i.e.*, [Fe(CN)<sub>6</sub>]<sup>4</sup>-

If the oxidation state of Fe in the complex is +3;

$$x = + 3 + 6 \times (-1)$$
  
= -3, i.e.,  $[Fe(CN)_6]^{3-}$ 

**Example 2.** Determine the oxidation state of metal in the complex ion,  $[PtCl_6]^{2-}$ .

**Solution.** Charge on the complex ion = Oxidation state of metal + charge on ligands

$$-2 = x + 6 \times (-1)$$
$$x = +4$$

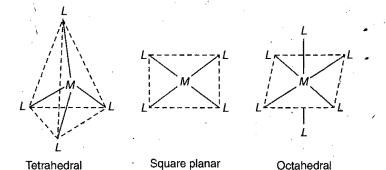
or

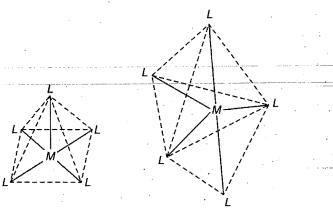
The oxidation state of Pt in the complex ion is +4.

#### 4. Coordination polyhedron

In the coordination sphere, the ligands attached to the central metal atom or ion occupy definite positions around the metal atom or ion in space giving a definite geometry to the complex ion or coordination entity. The spatial arrangement of the ligand atoms which are directly attached to the central atom or ion is called coordination polyhedron.

The generally observed coordination polyhedra are tetrahedral, square planar, octahedral, square pyramidal, and trigonal bipyramidal.





#### Square planar

Trigonal bipyramidal

#### ■ 5. Effective atomic number (EAN)

Ligands are attached with the central metal ion through donor atoms. Each donor atom donates one electron pair to the central metal ion, *i.e.*, the central metal atom or ion gains electrons from the donor atoms. In order to explain the stability of the complex, Sidgwick proposed **effective atomic number** abbreviated as EAN, which is defined as **the resultant number** of electrons with the metal atom or ion after gaining electrons from the donor atoms of the ligands. The effective atomic number (EAN) generally coincides with the atomic number of next inert gas in some cases. EAN is calculated by the following relation:

EAN = Atomic number of the metal – number of electrons lost in ion formation + number of electrons gained from the donor atoms of the ligands

The EAN values of various metals in their respective complexes are tabulated below:

Complex	Metal (Oxid. state)	At. No. of metal	Coordination number	Effective atomic number
K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	+2	26	6	$(26-2) + (6 \times 2) = 36$ [Kr]
[Cu(NH <sub>3</sub> ) <sub>4</sub> ]SO <sub>4</sub>	+2	29 .	. 4	$(29 - 2) + (4 \times 2) = 35$
[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	+3	27	6	$(27-3) + (6 \times 2) = 36$ [Kr]
Ni(CO) <sub>4</sub>	0	28	4	$(28 - 0) + (4 \times 2) = 36$ [Kr]
K <sub>2</sub> [Ni(CN) <sub>4</sub> ]	+2	28	4	$(28 - 2) + (4 \times 2) = 34$
K <sub>2</sub> [PtCl <sub>6</sub> ]	+4	78	6.	$(78 - 4) + (6 \times 2) = 86 [Rn]$

$K_3[Cr(C_2O_4)_3]$	+3	24	. 6	$(24 - 3) + (6 \times 2) = 33$
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	+3	26	6	$(26-3) + (6 \times 2) = 35$
K <sub>2</sub> [HgI <sub>4</sub> ]	+2	80	4	$(80-2) + (4 \times 2) = 86$ [Rn]
[Ag(NH <sub>3</sub> ) <sub>2</sub> ]Cl	+1	47	2	$(47-1) + (2 \times 2) = 50$
K <sub>2</sub> [PdCl <sub>4</sub> ]	+2	46	4	$(46 - 2) + (4 \times 2) = 52$

Just as the octet is useful in formulating the bonding in compounds of the light elements, the notion of an EAN provides a rough guide for bonding in coordination compounds. Quite a few, but not all, metals achieve the EAN of a noble gas through coordination (see above table). The EAN concept has been particularly successful for complexes of low valent metals (oxidation state  $\leq +2$ ).

#### 6. Homoleptic and heteroleptic complexes

Complexes in which a metal is bound to only one kind of donor groups, e.g.,  $[Cr(NH_3)_6]^{3+}$  are known as homoleptic. Other examples are : $[Fe(CN)_6]^{3-}$ ,  $[PtCl_4]^{2-}$ ,  $[HgI_4]^{2-}$  etc.

Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic. Examples are :  $[Co(en)_2Cl_2]^+$ ,  $[Cr(NH_3)_4Cl_2]^+$ ,  $[Fe(H_2O)_4(C_2O_4)]^+$ , etc.

#### 7. Homonuclear and polynuclear complexes

Complexes in which only one metal atom is present are known as homonuclear complexes. Complexes in which more than one metal atom is present are known as polynuclear complexes.

## 15.3 NOMENCLATURE OF COORDINATION COMPOUNDS

Since several thousands of complexes (coordination compounds) are known and the number is constantly increasing, it is necessary to adopt a uniform system of naming these compounds. The International Union of Pure and Applied Chemistry (IUPAC) published rules for the systematic naming of coordination compounds in 1957. Some modifications in these rules were made in 1962 and 1971.

However, trivial names for certain coordination compounds are still in use, e.g.,  $K_4[Fe(CN)_6]$  and  $K_3[Fe(CN)_6]$  are called as potassium ferrocyanide and potassium ferricyanide even today.

The following rules are adopted these days for naming all types of coordination compounds:

- (1) If a coordination compound is ionic, the name of cation is given first whether or not it is the complex ion followed by the name of the anion just like naming a simple salt. The names of cation and anion are separated by a space.
- (2) Within a complex ion, the ligands are named first followed by the metal ion.

#### Names of the Ligands

(i) Anionic ligands ending with -ide are named by replacing -ide with suffix -o or replacing -e by -o.

Anion	Symbol	Name as ligand
Chloride	ci-	Chlorido
Bromide	Br <sup>-</sup>	Bromido
Cyanide	$CN^-$	Cyano
Oxide	$O^{2-}$	Охо
Peroxide	$O_2^{2-}$	Peroxo
Hydroxide	OH-	Hydroxo
Sulphide	S <sup>2-</sup>	Sulphido -
Amide	$NH_2^-$	Amido
Nitride	$N^{3-}$	Nitrido
Phosphide	P <sup>3-</sup>	Phosphido

Ligands whose names end in -ite or -ate become -ito or -ato, i.e., by replacing the ending -e with -o.

Anion	Symbol	Name as ligand
Carbonate	$CO_3^{2-}$	Carbonato
Oxalate	$C_2O_4^{2-}$	Oxalato
Sulphate	$SO_4^{2-}$	Sulphato
Nitrate	$NO_3^-$	Nitrato
Sulphite	$SO_3^{2-}$	Sulphito
Acetate	CH <sub>3</sub> COO	Acetato
Nitrite	ONO-	(bonded through oxygen) Nitrito-o
	$NO_2^-$	(bonded through nitrogen) Nitrito-n
		or Nitro

(ii) Neutral ligands are called with the same names as their neutral molecules or with their special names, e.g.,

$$\begin{array}{c} C_6H_5N \text{ or } & \longrightarrow \text{Pyridine} \\ PH_3 & \longrightarrow \text{Phosphine} \\ (C_6H_5)_3P & \longrightarrow \text{Triphenylphosphine} \\ H_2N - CS - NH_2 & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$$

**Note:** In the case of poly-dentate amino ligands we use single 'm' in the spelling, *i.e.*, amine is written, *e.g.*,

iii) Positively charged ligands have suffix -ium.

NH<sub>4</sub><sup>+</sup> Ammonium; NO<sup>+</sup> Nitrosylium; NH<sub>2</sub>—NH<sub>3</sub><sup>+</sup> Hydrazinium; NO<sub>2</sub><sup>+</sup> Nitronium

(iv) If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek numbers such as di, tri, tetra, penta, hexa, etc.

However, when the name of the ligand includes a number, e.g., dipyridyl, ethylenediamine, then bis, tris, tetrakis are used in place of di, tri, tetra, etc.

(v) Order of naming ligands: When more than one type of ligands are present, they are named in alphabetical order without separation by hyphen. This rule has come in force after 1971 convention.

Note: In the old system, (i) the ligands are named in the order of negative, neutral and positive without separation by hyphens.
(ii) when there are several ligands of same kind, these are listed alphabetically.

For example, in the complex  $[Cr(NH_3)_4Cl(NO_2)]^+$ , the ligands are named in the order of ammine, chlorido and nitrito-N in accordance to new convention. However, according to old convention, the ligands are named in the order of chlorido, nitrito-N and ammine (first negative ligands in alphabetical order and then neutral ligand).

- (3) The oxidation state of the central metal is shown by Roman numeral in bracket immediately following its name.
- (4) Complex positive ions and neutral coordination compounds have no special ending but complex negative ions always end in the suffix -ate. In most of the cases, the suffix -ate is fixed to English names of the metals but in some cases -ate is fixed with Latin names of metals.

Name of components present in coordination sphere are written in continuum, e.g.,

K<sub>3</sub>[Fe(CN)<sub>5</sub>NO] Potassium pentacyanonitrosylferrate(II)

Continuum

Element	Metal as named in anionic complex
Cobalt	Cobaltate
Nickel	Nickelate
Chromium	Chromate
Iron	Ferrate
Copper	Cuprate
Silver	Argentate
Lead	Plumbate

Note: In the case of mercury we may use both mercurate and hydrazinate.

(5) The name of the neutral coordination compound is given in one word only as the name of Ni(CO)<sub>4</sub> is tetracarbonylnickel (0). The following examples will make the rules more clear.

#### Coordination compounds containing complex cationic ion:

$[Pt(NH_3)_6]Cl_4$	Hexaammineplatinum(IV) chloride
[CO(NH <sub>3</sub> ) <sub>4</sub> H <sub>2</sub> OCl]Cl	Tetra ammine a quo chlorido cobalt (III) chloride
$[Cu(en)_2]SO_4$	Bis (ethane-1,2-diamine) copper(II) sulphate
$\left[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2\right]^+$	Tetraaquodichloridochromium(III) ion
$[Fe(H_2O)_4(C_2O_4)]_2SO_4$	Tetraaquooxalatoiron(III) sulphate
[Cr(NH <sub>3</sub> ) <sub>4</sub> (ONO)Cl]NO <sub>3</sub>	Tetraamminechloridonitrito-o-chromium(III)
	nitrate
[Ag(NH <sub>3</sub> ) <sub>2</sub> ]CI	Diammine silver(I) chloride
[Co(NH <sub>3</sub> ) <sub>5</sub> (NCS)]Cl <sub>2</sub>	Pentaammineisothiocyanatocobalt(III)
	chloride
$[\{(C_6H_5)_3P\}_3Rh]Cl$	Tris (triphenylphosphine) rhodium(I)
	chloride

#### Coordination compounds containing complex anionic ion:

K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	Potassium hexacyanoferrate (II)
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	Potassium hexacyanoferrate (III)
$K_3[Cr(C_2O_4)_3]$	Potassium trioxalatochromate (III)
$K_3[Co(C_2O_4)_2Cl_2]$	Potassium dichloridodioxalatocobaltate (III)
$K_2[HgI_4]$	Potassium tetraiodidomercurate (II)
K <sub>2</sub> [PtCl <sub>6</sub> ]	Potassium hexachloridoplatinate (IV)
$Na[Ag(CN)_2]$	Sodium dicyanoargentate (I)
$[Ni(CN)_4]^{2-}$	Tetracyanonickelate(II) ion
$Na_3[Co(NO_2)_6]$	Sodium hexanitrocobaltate (III)
K <sub>3</sub> [Fe(CN) <sub>5</sub> NO]	Potassium pentacyanonitrosyl ferrate (II)

## Coordination compounds containing complex cationic and anionic ions:

$[Cr(NH_3)_6][Co(CN)_6]$	Hexaamminechromium (III)
	hexacyanocobaltate (III)
[Pt(NH <sub>3</sub> ) <sub>4</sub> ][CuCl <sub>4</sub> ]	Tetraammineplatinum (II)
	tetrachloridocuprate (II)
$[Cr(NH_3)_6][Co(C_2O_4)_3]$	Hexaamminechromium (III)
*	trioxalatocobaltate (III)
$[Pt(py)_4][PtCl_4]$	Tetrapyridine platinum (II)
	tetrachloridoplatinate (II)

#### Non-ionic coordination compounds:

Fe(CO) <sub>5</sub>	Pentacarbony	liron(0)
$[\mathrm{Co}(\mathrm{NO}_2)_3(\mathrm{NH}_3)_3]$	Triamminetri	nitro cobalt (III)
$Cu(Gly)_2$	Diglycinatoco	opper (II)
Ni(DMG)2	Bis (dimethyl	glyoximato) nickel (II)

(6) Bridging groups in bidentate ligands: In a polyatomic complex which contains two or more central metal ions, the ligands which act as bridge between two metal atoms, the Greek letter  $\mu$  (mu) separated by a hyphen is written before their names. For example, the complex

Bis (ethane-1,2-diamine) cobalt(III)-μ-amido-μ-hydroxo bis (ethane-1,2-diamine) cobalt(III) sulphate

Or

Tetrakis (ethane-1,2-diamine) - $\mu$ -amido- $\mu$ -hydroxodicobalt (III) sulphate.

The complex 
$$\left[ (H_2O)_4 Fe \middle\backslash OH \middle\rangle Fe(H_2O)_4 \right] (SO_4)_2 \text{ is }$$
 named as:

Tetraaquoiron(III) - u-dihydroxotetraaquoiron(III) sulphate.

## Writing the formula of a coordination compound from its IUPAC name

Following rules are followed in writing the formula of a coordination compound:

- 1. Formula of the cation whether simple or complex is written first, followed by that of an anion.
  - 2. The coordination sphere is written in square brackets.
- **3.** The following sequence of symbols within the coordination sphere is followed:
  - (i) Metal atom
- (ii) Anionic ligands
- (iii) Neutral ligands
- (iv) Cationic ligands
- (a) If there are a number of ligands of same type (anionic, neutral or cationic), they are listed alphabetically, according to first alphabet of their formula. For example, if NO<sub>3</sub>, SO<sub>4</sub><sup>2</sup>, OH<sup>-</sup>, Br<sup>-</sup>, etc., are present, they are written as Br<sup>-</sup>, NO<sub>3</sub>, OH<sup>-</sup> and SO<sub>4</sub><sup>2</sup>.
- (b) When two ligands have same defining atom, the ligand with fewer such atoms is cited first followed by the ligand having more atoms. For example,  $SO_4^{2-}$  precedes  $S_2O_3^{2-}$ .
- (c) When the number of defining atoms are same, subsequent, symbol decides the sequence. For example,  $NH_2^-$  precedes  $NO_2$  because H comes before O.
- **4.** Polyatomic ligands are enclosed in parentheses but all ligands are formulated without any space in between.
- 5. The number of cations or anions to be written in the formula is calculated on the basis that total positive charge on the cation must be equal to the total negative charge on the anion, as the complex as a whole is electrically neutral.
- 6. Sometimes abbreviations for certain ligands are used in parentheses instead of their structural formulae. For example,

(en)	ethylenediamine	(dmg)	dimethylglyoximato
	(ethane-1, 2-diamine)		•
(dien)	diethylenetriamine	(py)	pyridine (pyridyl)
(trien)	triethylenetetraamine	(phen)	1,10-phenanthroline
(acac)	acetylacetonato	(gly)	glycinato
(dipy)	dipyridyl	(tripy)	tripyridyl
(edta)	ethane-1,2-diamine	(ox)	oxalato
	tetraacetato		

Few examples are given here to explain the above rules.

#### 1. Potassium amminetrichloridoplatinate(II)

Cation:  $K^+$ ; Anion:  $[PtCl_3(NH_3)]^x$ 

x =oxid. number of Pt + algebraic sum of charges carried by ligands

$$= + 2 + 3 \times (-1) + 0 = -1$$

Thus, the charge on the complex anion is -1.

Therefore, the formula of the coordination compound is  $K[PtCl_3(NH_3)]$ 

#### 2. Tetraammineaquachloridocobalt(III) chloride

Cation: [CoCl(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>4</sub>]<sup>x</sup>

x =oxid. number of Co + algebraic sum of the charges on the ligands

$$= +3 + (-1) + 0 + 4 \times 0 = +2$$

 $Anion = Cl^{-}$ 

(Two anions neutralise the charge on the cation)
Therefore, the formula of the given coordination compound

#### 3. Tetraamminediaquacobalt(III) chloride

Cation :  $[Co(NH_3)_4(H_2O)_2]^x$ +3 + 0 + 0 = x

x = 3

: Molecular formula of the complex is:

 $[CO(NH_3)_4(H_2O)_2]Cl_3$ 

#### 4. Sodium ethane-1,2-diaminetetraacetatochromate(II)

Cation: Na<sup>+</sup>

Anion:  $[Cr(edta)]^x$ 

x = oxid. state of chromium + algebraic sum of charges on the ligands

$$= +2 + (-4) \times 1 = -2$$

Thus, two Na<sup>+</sup> ions should be present in the complex to neutralize the charge.

Therefore, molecular formula of the complex will be  $Na_2[Cr(edta)]$ 

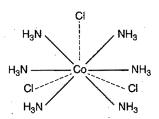
#### 15.4 WERNER'S COORDINATION THEORY

Werner, in 1893, proposed coordination theory to explain the properties and structures of various metal ammines of cobalt, chromium, platinum, etc. It was first successful attempt which satisfactorily described the formation of coordination compounds from stable molecules. The important postulates of coordination theory are:

- 1. Every element exhibits two types of valencies:
- (a) Primary valency and (b) Secondary valency.

In modern terminology, **primary valency** corresponds to the oxidation state of the central metal and secondary valency represents the coordination number of the metal. Primary valency is satisfied by negative ions. This is also called **principal**, **ionisable** or **ionic valency**. Its attachment to the metal is shown by dotted lines.

The secondary valency is satisfied by neutral molecules or negative ions. This valency is non-ionic or non-ionisable. The donor atoms of the ligands which satisfy the coordination number are directly attached to the metal atom and shown by thick lines. Thus, the coordination compound, CoCl<sub>3</sub>·6NH<sub>3</sub>, may be represented as:

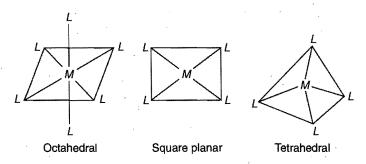


Every metal has a fixed coordination number. For example, Co(III) and Pt(IV) were recognised as having coordination number 6 while Cu(II) has 4. In order to designate materials held by secondary valencies, it has become customary to enclose the metal and all such materials in square bracket when writing formulae. For example, coordination compounds such as CoCl<sub>3</sub>·6NH<sub>3</sub> and PtCl<sub>4</sub>·6NH<sub>3</sub> are written as [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> and [Pt(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>4</sub> respectively.

2. Every element tends to satisfy both its primary and secondary valencies. A negative ion when present in the coordination sphere shows a dual behaviour. It may satisfy both primary and secondary valencies. The presence of negative ion in the coordination sphere reduces the charge on the complex ion by the amount of charge possessed by it and the negative ions present in the coordination sphere are not ionised. Thus, the following coordination compounds will have varying number of ionisable chlorine atoms but coordination number remains the same.

Coordination	Modern formula	Charge on the cation	Coordination number (secondary val.)	Primary valency	Total no. of ions
PtCl <sub>4</sub> ·6NH <sub>3</sub>	[Pt(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>4</sub>	+4	6	4	5
PtCl <sub>4</sub> ·5NH <sub>3</sub>	[Pt(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>3</sub>	+3	6	4	4
PtCl <sub>4</sub> ·4NH <sub>3</sub>	[Pt(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl <sub>2</sub>	+2	6	4.	3
$PtCl_{4} \cdot 3NH_{3}$	[Pt(NH <sub>3</sub> ) <sub>3</sub> Cl <sub>3</sub> ]Cl	+1	6	4	2
PtCl <sub>4</sub> ·2NH <sub>3</sub>	[Pt(NH <sub>3</sub> ) <sub>2</sub> Cl <sub>4</sub> ]	Ó	6	4	Non-electro- lyte

3. The ligands which satisfy the secondary valencies are directed towards fixed positions in space. The geometry of the complex ion depends on the coordination number. If the metal

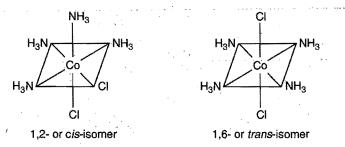


has coordination number 6, the complex is octahedral, *i.e.*, six positions around the metal are occupied by six donor atoms of the ligands octahedrally. On the other hand, if the coordination number is 4, the geometry of the complex may be tetrahedral or square planar. This postulate predicted the existence of different types of isomerism in coordination compounds.

#### **Examples:**

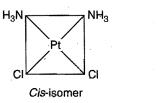
Octahedral	Square planar	Tetrahedral
$[Cr(NH_3)_6]^{3+};$	[Ni(CN) <sub>4</sub> ] <sup>2-</sup> ;	[Ni(CO) <sub>4</sub> ];
$[Co(NH_3)_6]^{3+};[Cr(H_2O)_6]^{3+};$	$[Ni(NH_3)_4]^{2+};$	$[CuX_4]^{2-}$ ; $[ZnCl_4]^{2-}$ ;
$[Fe(CN)_6]^{2-}; [Fe(F_6)]^{3-};$	$[Cu(NH_3)_4]^{2+};$	$[NiX_4]^{2-}$
$[Pt(NH_3)_6]^{4+}; [PtCl_6]^{2-}$	,	$X = Cl^-, Br^-, I^-$

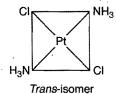
In [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl, Werner was able to isolate two isomers. He predicted an octahedral structure for coordination number 6, because only octahedral structure can form two isomers (l, 2- and 1, 6-). The planar hexagonal and trigonal prism arrangements will give three isomers each.



Similarly, the existence of two geometrical isomers of the complex, Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, was proved by accepting square planar configuration.

The postulates of Werner's coordination theory were actually based on experimental evidences rather than theoretical. A large number of metal ammines were studied by Werner using molar conductance values as to ascertain the number of ions per molecule and chemical methods such as precipitation of Cl<sup>-</sup> by AgNO<sub>3</sub> as to determine the number of ionisable Cl<sup>-</sup> ions per molecule. The following experimental data regarding cobalt ammines well supported the postulates that the secondary valency of 6 is maintained in all the cobalt ammines and when the Cl<sup>-</sup> ion enters the coordination sphere, it decreases the positive charge on the complex ion by one unit.





Molecular formula	Molar conductance	No. of ions in molecules	Ionisable Cl <sup>-</sup> ions (precipitation with AgNO <sub>3</sub> )	Secondary valency	Ionic formulation
CoCl <sub>3</sub> 6NH <sub>3</sub>	430	4	3	6	[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>
CoCl <sub>3</sub> 5NH <sub>3</sub> ·H <sub>2</sub> O	430	4	3	6	[Co(NH <sub>3</sub> ) <sub>5</sub> H <sub>2</sub> O]Cl <sub>3</sub>
CoCl <sub>3</sub> 5NH <sub>3</sub>	250	3	2	6	$[Co(NH_3)_5Cl]Cl_2$
CoCl <sub>3</sub> 4NH <sub>3</sub>	100	2 .	1	6 .	[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl
CoCl <sub>3</sub> 3NH <sub>3</sub>	0	Non-e	lectrolyte	6	[Co(NH <sub>3</sub> ) <sub>3</sub> Cl <sub>3</sub> ]

Werner theory is also supported by the conductance measurements.

In above complexes A, B, C and D, the primary valency is satisfied by 3, 2, 1 and 0, Cl<sup>-</sup> ions respectively. Thus, conductance of equimolar aqueous solution of these complex lie in following order:

## 15.5 ISOMERISM IN COORDINATION COMPOUNDS

The compounds having same molecular formula but different physical and chemical properties on account of different structures are called **isomers** and the phenomenon as **isomerism**. Isomerism in coordination compounds may be divided into two main types:

(1) Structural isomerism, (2) Stereo-isomerism

#### 1. Structural Isomerism

It is displayed by compounds that have different ligands within their coordination spheres. The different types of structural isomerism shown by coordination compounds are discussed below:

(i) Ionisation isomerism: This type of isomerism arises when the coordination compounds give different ions in solution. For example, there are two isomers of the formula Co(NH<sub>3</sub>)<sub>5</sub>BrSO<sub>4</sub>.

$$[\text{Co(NH}_3)_5\text{Br}]\text{SO}_4 \iff [\text{Co(NH}_3)_5\text{Br}]^{2+} + \text{SO}_4^{2-}$$
(Violet)

Pentaamminebromidocobalt(III) ion

This isomer gives a white precipitate of BaSO<sub>4</sub> with BaCl<sub>2</sub> solution.

$$[Co(NH_3)_5SO_4]Br \rightleftharpoons [Co(NH_3)_5SO_4]^+ + Br^-$$
(Red) Pentaamminesulphato-
cobalt(III) ion

Above isomer gives light yellow precipitate with AgNO<sub>3</sub> solution. Other examples of ionisation isomerism are:

[Pt(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Br <sub>2</sub> Tetraamminedichlorido- platinum(IV) bromide	and	[Pt(NH <sub>3</sub> ) <sub>4</sub> Br <sub>2</sub> ]Cl <sub>2</sub> Tetraamminedibromido- platinum(IV) chloride
[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]NO <sub>2</sub>	and	[Co(NH <sub>3</sub> ) <sub>4</sub> ClNO <sub>2</sub> ]Cl
Tetraamminedichlorido-		Tetraamminechloridonitrito-n-
cobalt(III) nitrite		cobalt(III) chloride

- (ii) Hydrate isomerism: This type of isomerism arises when different number of water molecules are present inside and outside the coordination sphere. This isomerism is best illustrated by the three isomers that have the formula CrCl<sub>3</sub>·6H<sub>2</sub>O.
- (a) [Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>—Violet. All the six water molecules are coordinated to Cr. It has three ionisable chloride ions.
- (b) [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub>·H<sub>2</sub>O—Green. Five water molecules are coordinated to Cr. It has two ionisable chloride ions. One water molecule outside the coordination sphere can be easily lost.
- (c)  $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$ —Green. Four water molecules are coordinated to Cr. It has one ionisable  $Cl^-$  ion. Other examples of hydrate isomerism are:

(iii) Coordination isomerism: This type of isomerism is observed in the coordination compounds having both cationic and anionic complex ions. The ligands are interchanged in both the cationic and anionic ions to form isomers. Some examples are:

[Pt(NH <sub>3</sub> ) <sub>4</sub> ][CuCl <sub>4</sub> ] Tetraammineplatinum(II) tetrachloridocuprate(II)	and	[Cu(NH <sub>3</sub> ) <sub>4</sub> ][PtCl <sub>4</sub> ] Tetraamminecopper(II) tetrachloridoplatinate(II)
$[Cr(NH_3)_6][Co(C_2O_4)_3] \\ Hexaamminechromium(III) \\ trioxalatocobaltate(III)$	and	[Co(NH <sub>3</sub> ) <sub>6</sub> ][Cr(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] Hexaamminecobalt(III) trioxalatochromate(III)

[Cr(NH<sub>3</sub>)<sub>6</sub>][Cr(SCN)<sub>6</sub>] Hexaamminechromium(III) hexathiocyanatochromate(III) and

[Cr(NH<sub>3</sub>)<sub>4</sub>(SCN)<sub>2</sub>][Cr(NH<sub>3</sub>)<sub>2</sub>(SCN)<sub>4</sub>]

Tetraamminedithiocyanatochromium(III) diamminetetrathiocyanatochromate(III)

(iv) Linkage isomerism: This type of isomerism occurs in complex compounds which contain **ambidentate** ligands like  $NO_2^-$ ,  $SCN_2^-$ ,  $CN_2^-$ ,  $S_2O_3^{2-}$  and CO. These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex. These types of isomers are distinguished by infra-red (I.R.) spectroscopy. For example,  $[Co(NH_3)_5NO_2]Cl_2$  and  $[Co(NH_3)_5ONO]Cl_2$  are linkage isomers as  $NO_2^-$  is linked through N or through O.

and

and

[Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>]Cl<sub>2</sub> Pentaamminenitrito-*n*-cobalt(III) chloride (yellow) [Co(NH<sub>3</sub>)<sub>5</sub>ONO]Cl<sub>2</sub> Pentaamminenitrito-o-cobalt(III)

chloride (red)

Another example of this type of isomerism is:

[Pd(dipy)(SCN)<sub>2</sub>] Dipyridyldithiocyanatopalladium(II) [Pd(dipy)(NCS)<sub>2</sub>] Dipyridyldiisothiocyanatopalladium(II)

(v) Polymerisation isomerism: This type of isomerism exists in compounds having same stoichiometric composition but different molecular compositions. The molecular compositions are simple multiples of the simplest stoichiometric arrangement. For example in the following three compounds, the second and third compounds are polymers of the first.

[Note: (ii) and (iii) compounds are actually not the examples of polymerisation, *i.e.*, (i) compound is not acting as a monomer in the formation of (ii) and (iii) compounds.]

(vi) Coordination position isomerism: This type of isomerism is exhibited by polynuclear complexes by changing the position of ligands with respect to different metal atoms present in the complex. For example,

$$\begin{bmatrix} (NH_3)_4 Co & NH_2 \\ O_2 & Co(NH_3)_2 Cl_2 \end{bmatrix}^{24}$$
Unsymmetrical

(Both the chloro ligands are with same cobalt ion.)

and  $\left[ (NH_3)_3 ClCo \bigvee_{O_2} NH_2 Co(NH_3)_3 Cl \right]^{2+}$ Symmetrical

(Same ligands are linked with both cobalt ions.)

#### 2. Stereo-isomerism

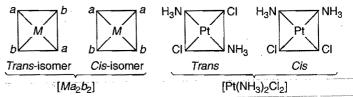
Compounds are stereo-isomers when they contain the same ligands in their coordination spheres but differ in the way that these ligands are arranged in space. Stereo-isomerism is of two types, *viz.*, geometrical isomerism and optical isomerism.

(1) Geometrical isomerism: This isomerism is due to ligands occupying different positions around the central metal atom or ion. The ligands occupy positions either adjacent or opposite to one another. This type of isomerism is also known as *cis*- and *trans*- isomerism.

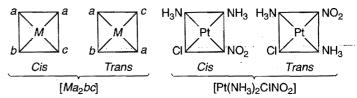
Geometrical isomerism is very much common in coordination number 4 and 6 complexes.

**Square planar complexes** (coordination number four) exhibit geometrical isomerism.

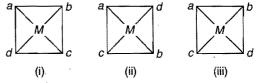
(i) Complexes with general formula,  $Ma_2b_2$  (where both a and b are monodentate) can have cis- and trans-isomers.



(ii) Complexes with general formula,  $Ma_2bc$  can have *cis*-and *trans*-isomers.



(iii) Complexes with general formula, *Mabcd* can have three isomers.



**Example:**  $[Pt(NH_3)(NH_2OH)(NO_2)(py)]NO_2$ .

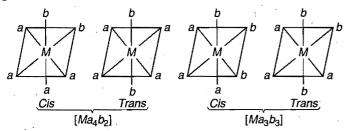
(iv) Square planar complexes having unsymmetrical bidentate ligands can also show geometrical isomerism. For example, platinum glycinato complex, [Pt(Gly)<sub>2</sub>], exhibits geometrical isomerism.

 $[Ma_4]^{n\pm}$  and  $[Ma_3b]^{n\pm}$  type square planar complexes do not show geometrical isomerism.

#### Tetrahedral and Linear complexes

These complexes do not show geometrical isomerism because the geometry of these ligands is definite, *e.g.*, in tetrahedral complexes, any two ligands lie at 109°28'; while in linear complexes, the two ligands lie at 180°.

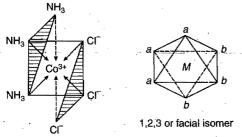
Octahedral complexes of the type  $Ma_4b_2$  and  $Ma_3b_3$  exhibit geometrical isomerism.



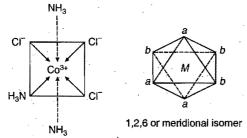
**Example:** [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl, [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>] Octahedral complexes of general formula, *Mabcdef*, can have fifteen geometrical isomers.

#### Facial and Meridional Isomers

A set of three ligands (similar) may be arranged on an octahedron in all *cis*-fashion, giving facial or 'fac' isomer. In other words, three similar ligands on the same face of octahedron give rise to the facial isomer.



A set of three similar ligands may be arranged on an octahedron with one pair *trans* (meridian of octahedron), giving rise to meridional or 'mer' isomer.



**Note:** 1. Geometrical isomerism is not observed in complexes of coordination number 2 and 3.

- Geometrical isomerism is not observed in complexes of coordination number 4 of tetrahedral geometry.
- 3. The complexes of general formulae,  $Ma_3b$  or  $Mab_3$ , or  $Ma_4$ , of square planar geometry do not show geometrical isomerism.
- 4. The complexes of general formulae,  $Ma_6$  and  $Ma_5b$ , of octahedral geometry do not show geometrical isomerism.
- 'Fac' and 'mer' isomers of an [Ma<sub>3</sub>b<sub>3</sub>] octahedral complex are optically inactive.

(2) Optical isomerism: A coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have same formula but differ in their abilities to rotate directions of the plane of polarised light are said to exhibit optical isomerism and the

molecules are optical isomers. The optical isomers are pair of molecules which are non-superimposable mirror images of each other. The essential requirement for a substance to be optically active is that the substance should not have a plane of symmetry in its structure. The isomer which rotates the plane of polarised light to right direction is termed dextro (d-form) while the isomer which rotates the plane of polarised light to left direction is termed laevo (l-form). The two optically active isomers are collectively called enantiomers. Enantiomers are mirror image to each other and their physical properties are different.

Optical isomerism is expected in tetrahedral complexes of the type *Mabcd* but no optical isomer has been isolated until now.

However, compounds containing two unsymmetrical bidentate ligands have been resolved into optical isomers and are known for Be(II), Zn(II) and B(III). For example, Bis-benzoylacetonato-beryllium(II) exhibits optical isomerism.

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Optical isomers rarely occur in square planar complexes on account of the presence of axis of symmetry.

Optical isomerism is very common in octahedral complexes. Octahedral complexes of general formulae,

$$[Ma_2b_2c_2]^{n\pm}$$
,  $[Mabcdef]$ ,  $[M(AA)_3]^{n\pm}$ ,  $[M(AA)_2a_2]^{n\pm}$ , (where  $AA$  = symmetrical bidentate ligands)

$$[M(AA)_2ab]^{n\pm}$$
 and  $[M(AB)_3]^{n\pm}$ 

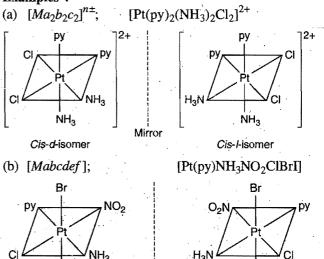
(where AB unsymmetrical ligands)

I-isomer

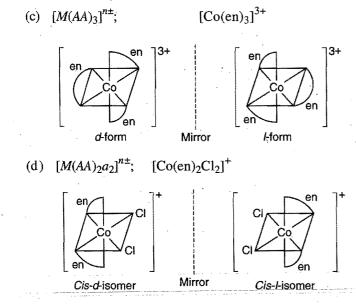
show optical isomerism.

d-isomer

#### Examples:

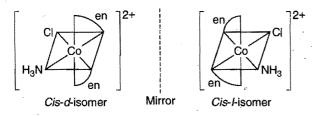


Mirror

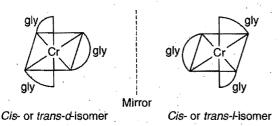


Trans form of  $[M(AA)_2a_2]^{n\pm}$  does not show optical isomerism.

(e)  $[M(AA)_2ab]^{n\pm}$ ;  $[Co(en)_2NH_3Cl]^{2+}$ 



(f)  $[M(AB)_3]$ ;  $[Cr(gly)_3]$ 



Some more examples are:

 $[Cr(ox)_3]^{3-}$ ;  $[Fe(dipy)_3]^{2+}$ ;  $[Cr(ox)_2(H_2O)_2]^-$ ;  $[Pt(en)_3]^{4+}$ 

## 15.6 BONDING IN COORDINATION COMPOUNDS

Werner was first to describe the structures and the existence of various types of isomerism in coordination compounds. However, the nature of bonding between central metal atom and ligands in the coordination sphere has been explained by the three well-known theories. These theories are:

- 1. Valence bond theory
- 2. Crystal field theory
- 3. Ligand field or molecular orbital theory

#### 

It is the simplest of the three theories and was developed mainly by Pauling. It describes the bonding in terms of hybridized orbitals of the central metal atom or ion. The theory mainly deals with the geometry (*i.e.*, shape) and magnetic properties of the complexes. The salient features of the theory are:

- (i) The central metal loses a requisite number of electrons to form the ion. The number of electrons lost is the valency of the resulting cation. In some cases, the metal atom does not lose electrons.
- (ii) The central metal ion or atom (as the case may be) makes available a number of empty s-, p- and d-atomic orbitals equal to its coordination number. These vacant orbitals hybridize together to form hybrid orbitals which are same in the number as the atomic orbitals hybridizing together. They are vacant, equivalent in energy and have definite geometry.

Some of the common hybridized orbitals met in the coordination compounds are listed below:

(For details see chapter 2 on valency.)

Coordi- nation number	Type of hybri- dization	Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$ , $[Ag(CN)_2]^-$
3 .	$\frac{sp^2}{sp^3}$	Trigonal planar	[HgI <sub>3</sub> ]
4	$sp^3$	Tetrahedral	$Ni(CO)_4$ , $[Ni(X_4)]^{2-}$ , $[ZnCl_4]^{2-}$ ,
	dsp <sup>2</sup>	Cayana planas	$[CuX_4]^2$ , where $X = C\Gamma$ , Br, $\Gamma$ $[Ni(CN)_4]^2$ , $[Cu(NH_3)_4]^2$
*	asp	Square planar	$[Ni(NH_3)_4]^{2+}$
5	$dsp^3$	Trigonal bipyramidal	Fe(CO) <sub>5</sub> , $[CuCl_5]^{3-}$
	$sp^3d$	Square pyramidal	[SbF <sub>5</sub> ] <sup>2-</sup>
6	1	Octahedral	$[Cr(NH_3)_6]^{3+}$ , $[Fe(CN)_6]^{3-}$
	$sp^3d^2$	(Inner orbital) (Outer orbital)	$[FeF_6]^{3-}$ , $[Fe(H_2O)_6]^{2+}$ , $[Ni(NH_3)_6]^{2+}$

- (iii) The non-bonding electrons of the metal occupy the inner orbitals. These are grouped in accordance with Hund's rule, however, under the influence of some strong ligands, there may be some re-arrangement of electrons in the atomic orbitals (against Hund's rule). The d-orbitals participating in this process of hybridization may be either (n-1)  $d^2sp^3$  or  $nsp^3d^2$ . The complexes thus formed are referred to as inner or low spin and outer or high spin complexes, respectively.
- (iv) The ligands have at least one  $\sigma$ -orbital containing a lone pair of electrons. Vacant hybrid orbitals of the metal atom or ion overlap with the  $\sigma$ -orbitals containing lone pair or electrons of the ligands to form  $M \leftarrow$  ligand  $\sigma$ -bond. This bond is called coordinate bond (a special type of covalent bond) and possesses a considerable amount of polarity.

(v) It is possible to predict the magnetic properties of the complex if the geometry of the complex ion (or *vice-versa*) is known. If the complex contains unpaired electrons, it is paramagnetic in nature whereas if it does not contain unpaired electrons, *i.e.*, all are paired, the complex is diamagnetic in nature. Complexes having unpaired electron are coloured.

The number of unpaired electrons and the geometries of the complex ions having central metal ion with configurations  $d^1$  to  $d^9$  are related to each other as shown below:

The shapes and magnetic nature of some of the common complexes of metals of 3d-series have been described on the basis of valence bond theory in the table given below:

	Number of unpaired electrons for different geometries					
$d^x$ Configuration	T. 4. 1. 1. (3)	S (1, 2)	Octahedral			
	Tetrahedral (sp <sup>3</sup> )	Square planar (dsp <sup>2</sup> )	Inner orbitals (d <sup>2</sup> sp <sup>3</sup> )	Outer orbitals $(sp^3d^2)$		
$d^1$	1	. 1	1	1		
$d^2$	2	2	2	2		
$d^3$	3	3	3	3		
$d^4$	4	4	2	4		
$d^{5}$		3	1	5		
$d^6$	4	2	0	4		
$d^7$	3	1	1	3		
			(Shifted to higher orbits)			
<i>d</i> <sup>8</sup>	2	0		2		
		×	(2 electrons shifted)			
$d^9$	1	1 .	1	1		
		(Shifted)	(3 electrons shifted)			

Limitations of valence bond theory: The valence bond theory was fairly successful in explaining qualitatively the geometry and magnetic properties of complexes. However, it has a number of limitations.

- (i) The theory does not offer any explanation about the spectra of complex (why most of the complexes are coloured).
- (ii) Sometimes the same metal ion assumes different geometry when formation of complex ion takes place. The theory is unable to explain why at one time the electrons are rearranged against the Hund's rule while at other times the electronic configuration is not disturbed.
  - (iii) The theory does not offer an explanation for the existence of inner-orbital and outer-orbital complexes.
  - (iv) The theory does not explain why certain complexes are labile while others are inert.
- (v) In the formation of  $[Cu(NH_3)_4]^{2+}$ , one electron is shifted from 3d to 4p-orbital. The theory is silent about the energy availability for shifting such an electron. Such an electron can be easily lost, then why  $[Cu(NH_3)_4]^{2+}$  complex does not show reducing properties.
  - (vi) The changes in energies of the metal orbitals on formation of complex are difficult to calculate mathematically.

Inner orbital octahedral complexes or low spin complexes	Outer orbital octahedral complexes or high spin complexes		
<ol> <li>These complexes are formed by hybridization of d<sup>2</sup>sp<sup>3</sup> hybridisation.         These are formed by strong ligands.     </li> <li>These complexes generally possess less number of unpaired electrons i.e., they show either low or no magnetic moment.</li> <li>These are less reactive i.e., more stable. Substitution reactions are difficult to occur.</li> </ol>	<ol> <li>These complexes are formed by hybridisation of sp<sup>3</sup>d<sup>2</sup> hybridisation. These are formed by weak ligands.</li> <li>These complexes generally possess greater number of unpaired electrons i.e., they show high magnetic moment.</li> <li>These are reactive i.e., less stable. Substitution reactions are easy to occur.</li> </ol>		

Note: (i)  $M^{n+}$  ions which have one, two or three electrons in 3d orbitals prefer to form inner orbital octahedral complexes.

- (ii)  $M^{n+}$  ions which have  $d^8$  and  $d^9$  configurations prefer to form outer orbital octahedral complexes.
- (iii)  $M^{n+}$  ions which have  $d^4$ ,  $d^5$  and  $d^6$  configurations may form either inner or outer orbital complexes. It depends on the nature of the ligand.
- (iv) M<sup>n+</sup> (Pt<sup>2+</sup>, Pd<sup>2+</sup>, Ni<sup>2+</sup>, Au<sup>3+</sup>, etc.) having d<sup>8</sup> configuration mainly form square planar complexes.
- (v)  $M^{n+}$  having  $d^0$ ,  $d^5$  and  $d^{10}$  configurations prefer to form tetrahedral complexes.

#### (2) Crystal field theory

Crystal field theory was proposed by H. Bethe (1929) and Van Vleck (1932) and was originally applied to ionic crystals to explain their optical properties and is, therefore, called **crystal field theory**. However, this theory was applied to the study of coordination compounds in 1950. The valence bond theory represents the ligand metal bond as covalent, with an electron pair, shared between the metal and the ligand donor atom. The valence bond theory is frequently used but it is not adequate to explain properties of complexes such as colour and magnetism. Currently, the bonding in coordination complexes is usually described by crystal field theory or ligand field theory. This theory accounts for more satisfactory explanation for the properties of complexes especially colour and magnetism. The main points of the theory are:

(i) According to crystal field theory, the bonding in complex ions is purely electrostatic. This theory regards the ligand atoms of ionic ligands such as F<sup>-</sup>, Cl<sup>-</sup> or CN<sup>-</sup> as negative point charges (also called point charges) and if the ligand molecules are neutral, these are regarded as point dipoles or simply dipoles, the negative end pointing towards central metal ion.

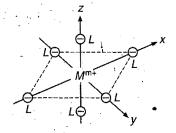
- (ii) The complex is regarded as a combination of a central metal ion surrounded by ligands which act as point charges or point dipoles. The arrangement of ligands around the central metal ion or atom is such that the repulsion between these negative points or dipoles is minimum.
- (iii) Interactions between positively charged nucleus of the central metal ion or atom and the negatively charged ligands are of two types:
- (a) The attractive forces arise due to the positive metal ion and the negatively charged ligands or the negative end of a polar neutral molecules. For example, in the case of complex ion,  $[Fe(CN)_6]^{3-}$ , the interactions are between  $Fe^{3+}$  ion and negatively charged  $CN^-$  ions whereas in the complex;  $[Cr(NH_3)_6]^{3+}$ , the interactions are between  $Cr^{3+}$ ion and

negatively charged ends of ammonia molecules. These attractive forces bind the ligands to the metal ion. The bonds between metal and the surrounding ligands are purely ionic. This theory does not consider any orbital overlapping.

- (b) The repulsive forces arise between the lone pairs on the ligands and electrons in the d-orbitals of the metal or atom. The crystal field theory mainly focuses on these repulsive forces. These forces are responsible for causing a considerable effect on the relative energies of the d-orbitals of the central metal ion or atom.
- (iv) In a free transition metal or ion, there are five d-orbitals which are designated as  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zz}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ . The five d-orbitals are divided into two sets depending on the nature of their orientation in space.
- (a) The three *d*-orbitals  $(d_{xy}, d_{yz}, d_{zx})$  which orient in the regions between the coordinate axes are designated as  $t_{2g}$  orbitals (pronounced as "t-two-g").  $t_{2g}$ -orbitals are three-fold degenerate. These are non-axial orbitals.
- (b) The other two orbitals  $(d_{\chi^2-\chi^2})$ ,  $d_{\chi^2}$  which orient along the axes are called  $e_g$ , orbitals (pronounced as "e-g").  $e_g$ , orbitals are two fold degenerate. These are also called axial-orbitals.

[The names  $t_{2g}$  and  $e_g$  are derived from spectroscopic terms.] In a free transition metal ion or atom, all the five d-orbitals have same energy, *i.e.*, they are degenerate. However, when the ligands approach the central metal ion or atom, the electrons of the d-orbitals of the central metal ion or atom are repelled by lone pairs of the ligands. As a result of these interactions, the degeneracy of d-orbitals of the metal ion is lost depending on the orientation of ligands in space. The d-orbitals split into two sets of orbitals having different energies. This is called crystals field splitting. It is the basis of crystal field theory. The extent of splitting depends on the number of ligands and their position around the metal atom or ion. The splitting is different in different structures with different coordination numbers.

**Splitting of** *d***-orbitals in octahedral complexes:** Let us consider an octahedral complex,  $[ML_6]^{n+}$ , in which the central metal ion is placed at the centre of the octahedron and is surrounded by six ligands which reside at the six corners of the octahedron as shown below.



The electrons in d-orbitals of the metal cation are repelled by negative point charge or by the negative end of the dipole of the ligands. This repulsion increases the energy of all the five d-orbitals. If all the ligands approaching the metal cation are at an equal distance from each of d-orbitals (i.e., the ligand field is spherically symmetrical), the energy of each of the five

## Geometry (shape) and magnetic nature of some of the complexes (Application of valence bond theory)

Atom / ion / complex	Configuration	Oxidation state of metal	Type of hybridi- zation	Geometry shape	No. of unpaired electrons	Magnetic nature
(1)	(2)	. (3)	(4)	(5)	- (6)	(7)
Ni <sup>2+</sup> (d <sup>8</sup> )	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	+2			2	Paramagnetic
[NiCl <sub>4</sub> ] <sup>2-</sup>	$\frac{1}{1}\frac{1}\frac$	+2	$sp^3$	Tetrahedral	2	Paramagnetic
[Ni(CN) <sub>4</sub> ] <sup>2+</sup>	Rearrangement $dsp^2$	+2	dsp <sup>2</sup>	Square planar	0	Diamagnetic
Ni		0			2	Paramagnetic
Ni(CO) <sub>4</sub>	Rearrangement $sp^3$	0	· sp <sup>3</sup>	Tetrahedral	0	Diamagnetic
[Ni(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	+2	$sp^3d^2$ (Outer)	Octahedral	2	Paramagnetic
Mn <sup>2+</sup> (d <sup>5</sup> )	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	+2			5	Paramagnetic
[Mn(CN) <sub>6</sub> ] <sup>4-</sup>	Rearrangement $d^2sp^3$	+2	$\begin{vmatrix} d^2sp^3 \\ (Inner) \end{vmatrix}$	Octahedral	1	Paramagnetic
[MnCl <sub>4</sub> ] <sup>2-</sup>	$\underbrace{\hspace{1cm} \vdots \hspace{1cm} \vdots$	+2	$sp^3$	Tetrahedral	5	Paramagnetic
Cu <sup>2+</sup> (d <sup>9</sup> )	<u>+++++++++</u>	+2			1.	Paramagnetic
[CuCl <sub>4</sub> ] <sup>2-</sup>	$\begin{array}{c} \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \\ \hline sp^3 \end{array}$	+2	$sp^3$	Tetrahedral	.1	Paramagnetic
[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>	$\frac{1}{dsp^2}$	+2	dsp <sup>2</sup>	Square planar	1 .	Paramagnetic
,	One electron is shifted from 3d- to 4p-orbital					

Contd. ...

(1)	(2)	(3)	(4)	(5)	(6)	(7)
$\operatorname{Cr}^{3+}(d^3)$	3d $4s$ $4p$	+3			3	Paramagnetic
[Cr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	$\frac{1}{d^2sp^3}$	+3	$d^2sp^3$ (Inner)	Octahedral	3	Paramagnetic
[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	$\begin{array}{c c} & 4d \\ \hline & \vdots & \vdots & \\ \hline & sp^3d^2 \end{array}$	+3	$sp^3d^2$ (Outer)	Octahedral	3	Paramagnetic
Co <sup>3+</sup> (d <sup>6</sup> )		+3			4	Paramagnetic
[CoF <sub>6</sub> ] <sup>3-</sup>	$sp^3d^2$	+3	sp <sup>3</sup> d <sup>2</sup> (Outer)	Octahedral	4	Paramagnetic
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	Rearrangement $d^2sp^3$	+3	$d^2sp^3$ (Inner)	Octahedral	0	Diamagnetic
$Co^{2+}(d^7)$		+2			3	Paramagnetic
[Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	$\frac{1}{sp^3d^2}$	+2	$sp^3d^2$ (Outer)	Octahedral	3	Paramagnetic
Fe <sup>2+</sup> (d <sup>6</sup> )		+2			4	Paramagnetic
[Fe(CN) <sub>6</sub> ] <sup>4</sup>	Rearrangement $d^2sp^3$	+2	$d^2sp^3$ (Inner)	Octahedral	0	Diamagnetic
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	$\frac{1}{sp^3d^2}$	+2	$sp^3d^2$ (Outer)	Octahedral	4	Paramagnetic
[Fe(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	Same	+2	sp <sup>3</sup> d <sup>2</sup> (Outer)	Octahedral	4	Paramagnetic
Fe <sup>3+</sup> (d <sup>5</sup> )		+3			5	Paramagnetic
[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	$\frac{1}{d^2sp^3}$	+3	$d^2sp^3$ (Inner)	Octahedral	1	Paramagnetic
Fe	11111111111	0		*.	4	Paramagnetic
Fe(CO) <sub>5</sub>		0	dsp <sup>3</sup> (Inner)	Trigonal bipyramidal	. 0	Diamagnetic

d-orbitals increases by the same amount, *i.e.*, all the d-orbitals remain degenerate, although they possess higher energy. However, this is not possible as it is only hypothetical situation.

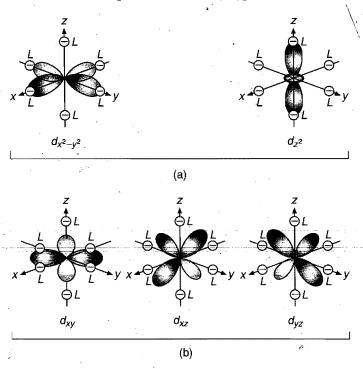
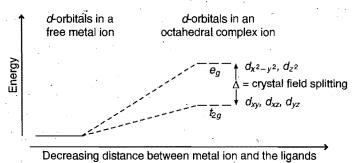


Fig. 15.1 The shapes of the five *d*-orbitals and their orientations with respect to an octahedral array of charged ligands

As the lobes of the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals [Fig. 15.1(a)] point directly towards the ligands, an electron in either of these orbitals is nearer to the electron pairs of the ligands than if it was in a  $d_{xy}$ ,  $d_{xz}$  or  $d_{yz}$  orbitals, with lobes pointing between the ligands [Fig. 15.1(b)]. Thus, the repulsions between the ligands and the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals are greater than the repulsions between the ligands and  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals. Consequently, the energies of  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals are



**Fig. 15.2 (i)** The changes in the energies of the *d*-orbitals of a metal ion as an octahedral complex is formed. As the ligands approach the metal ion, the initially degenerate *d*-orbitals split into two new sets of degenerate orbitals.

higher than the energies of  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals. Therefore, it is clear that introduction of the ligands removes the degeneracy of the five d-orbitals, splitting them into two sets of degenerate orbitals; the lower energy set consists of the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals and higher energy set comprises the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals [Fig. 15.2 (i)]. The three lower energy orbitals are collectively called the  $t_{2g}$  orbitals while the two higher energy orbitals are called  $e_g$  orbitals.

Thus, an energy difference exists between two sets of orbitals. This energy difference is called **crystal field splitting energy** (CFSE) or **crystal field stabilization energy** and is

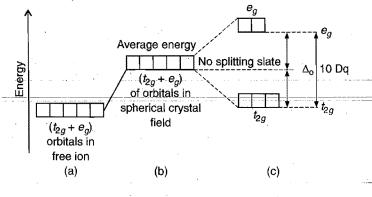


Fig. 15.2 (ii) Crystal field splitting of d-orbitals in an octahedral complex (a) Five degenerate d-orbitals of free metal cation

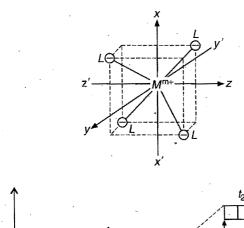
- (b) Hypothetical degenerate *d*-orbitals at higher energy level under spherically symmetrical ligand field
- (c) Splitting of d-orbitals under the influence of ligands.

represented by  $\Delta_o$  (the subscript o stands for octahedral). It measures the crystal field strength of the ligands. The crystal field splitting occurs in such a way that average energy of the d-orbitals does not change.

Thus, three orbitals lie at an energy that is  $-\frac{2}{5}\Delta_0$  below the average d-orbital energy and two d-orbitals lie at an energy  $+\frac{3}{5}\Delta_0$  above the average energy. The energy gap between  $t_{2g}$  and  $e_g$  sets is also denoted by 10 Dq. Energy of  $t_{2g}$  orbitals is 4 Dq less than that of hypothetical degenerate d-orbitals and that of  $e_g$  orbitals is 6 Dq above that of the hypothetical degenerate d-orbitals. Thus,  $t_{2g}$  set loses an energy equal to -0.4  $\Delta_0$  or -4 Dq while  $e_g$  set gains an energy equal to +0.6  $\Delta_0$  or +6 Dq.

Crystal field splitting in tetrahedral complexes: The tetrahedral arrangement of four ligands surrounding the metal ion  $M^{m+}$  may be depicted as shown in Fig. 15.3.

The three *d*-orbitals, *i.e.*,  $t_{2g}$  orbitals are close to the approaching ligands. As a result of this, the  $t_{2g}$  electrons suffer more repulsion than  $e_g$  electrons. The energy of  $t_{2g}$  orbitals increases more than  $e_g$  orbitals. The splitting is shown in Fig. 15.3.



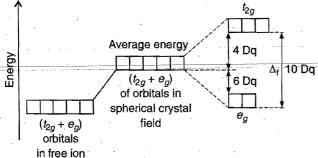


Fig. 15.3 Crystal field splitting of d-orbitals in a tetrahedral complex

The energy gap between two sets of orbitals is designated as  $\Delta_t$  (The subscript t indicates tetrahedral complex). It is observed that  $\Delta_t$  is considerably less than  $\Delta_0$ . It has been found that,

$$\Delta_t = \frac{4}{9} \Delta_0$$

Crystal field splitting in square planar complexes: The square planar arrangement of four ligands surrounding the metal ion may be considered as derived from octahedral by removing two ligands from z-axis. On account of removing negative charges from z-axis,  $d_{z^2}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals having z-component become more stable. As the lobes of  $d_{x^2-y^2}$  point towards the ligands, the orbital has highest energy and the lobes of  $d_{xy}$  orbital lie between the ligands, it is thus next highest in energy. The lobes of  $d_{xz}$  and  $d_{yz}$  are least affected by electrostatic field of the ligands as they lie out of the plane

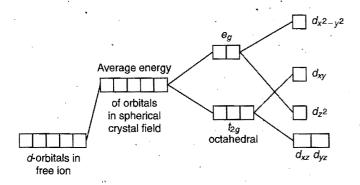


Fig. 15.4 Splitting of d-orbitals in square planar complex

of the complex. The lobes of  $d_{z^2}$  orbital lie out of the plane but the belt around the centre of the orbital lies in the plane of the complex is somewhat affected by electrostatic field of the ligands. The splitting of d-orbitals in square planar complex can be depicted as shown in Fig. 15.4.

Spectrochemical series: For any given metal cation, the magnitude of crystal field splitting energy depends on the nature of the ligands. The greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it. The ligands which affect only a small degree of crystal field splitting are termed weak field ligands while those which affect a large splitting are called strong field ligands.

When the ligands are arranged in order of the magnitude of crystal field splitting, the arrangement, thus, obtained is called spectrochemical series.

$$I < Br < CI < NO_3 < F < OH < OX^2 < H_2O < py$$
Weak field ligands

Increasing crystal field

 $I = NH_2 < en < dipy < c_Phen < NO_3 < CN < CO_3$ 

$$= NH_3 < en < dipy < o-Phen < NO_2 < CN < CO$$
Strong field ligands

From the above arrangement it is clear that ligands before  $H_2O$  such as  $I^-$ ,  $NO_3^-$ ,  $OH^-$ , etc., are weak field ligands while the ligands after  $H_2O$  such as  $NO_2^-$ ,  $CN^-$ , CO, etc., are strong field ligands. Stronger field ligands cause greater crystal splitting *i.e.*,  $\Delta_0$  value for octahedral complex is high.

Besides the nature of ligands, there are some other factors which affect the crystal field splitting energy. These factors are:

- (i) The position of transition metal in the periodic table: The magnitude of  $\Delta_0$  increases in going down a group, i.e., an ion of an element in the first transition series has a smaller value of  $\Delta_0$  than the ion of a heavier member of the same group. Thus, comparing complexes of  $\mathrm{Ni}^{2+}$  and  $\mathrm{Pt}^{2+}$  with the same ligand, it is observed that platinum complexes have larger crystal field splitting. The crystal field splitting,  $\Delta_{\overline{0}}$ , is about 50% higher for second transition series compared to the first whereas the third series in about 25% higher than second. There is small increase in the crystal field splitting along each series.
- (ii) The oxidation state of the metal: Generally, the higher the oxidation state of the metal, the greater the crystal field splitting. For example, most of the cobalt (II) complexes have low values of  $\Delta$  whereas all cobalt (III) complexes have high values of  $\Delta$ .
- (iii) The number of ligands: The crystal field splitting for a tetrahedral environment is about 4/9 that for an octahedral environment.

**Distribution of** d**-electrons in**  $t_{2g}$  **and**  $e_g$  **orbitals in octahedral complexes:** The distribution of d-electrons in  $t_{2g}$  and  $e_g$  orbitals takes place on the basis of the nature of ligands. Two cases may arise.

when the ligands are weak: Under the influence of weak ligands, the energy difference,  $\Delta_0$ , between  $t_{2g}$  and  $e_g$  sets is relatively small and hence all the five d-orbitals may be supposed to be degenerate, *i.e.*, all the d-orbitals have nearly the same energy and the distribution of electrons in  $t_{2g}$  and  $e_g$  sets occurs according to Hund's rule, *i.e.*, electrons will pair up only when each of the five d-orbitals is at least singly occupied. When the ligands are weak, the first three electrons numbered 1, 2, 3 go to  $t_{2g}$  set, those numbered 4, 5 go to  $e_g$  set, those numbered 6, 7, 8 go to  $t_{2g}$  set and the remaining two electrons numbered 9, 10 will occupy  $e_g$  set. This can be shown as:

$$t_{2g}^{1, 2, 3} \longrightarrow e_g^{4, 5} \longrightarrow t_{2g}^{6, 7, 8} \longrightarrow e_g^{9, 10}$$

In complexes of weak ligands,  $\Delta_0$  is less than P (P is called average pairing energy which is the energy required to pair two electrons in the same orbital).  $\Delta_0$ , the octahedral crystal field splitting energy, tends to force as many electrons to  $t_{2g}$  set while P tends to prevent the electrons to pair in the  $t_{2g}$  level.

(ii) When the ligands are strong: Under the influence of strong ligands, the energy difference between  $t_{2g}$  and  $e_g$  sets is relatively high and thus the distribution of d electrons in  $t_{2g}$  and  $e_g$  sets does not obey Hund's rule. The first electrons numbered 1, 2, 3, 4, 5, 6 will go to  $t_{2g}$  set and remaining four electrons numbered 7, 8, 9 and 10 will go to  $e_g$  set.

$$t_{2g}^{1, 2, 3, 4, 5, 6} \longrightarrow e_g^{7, 8, 9, 10}$$

For these complexes,  $\Delta_0$  is higher than P. The above points are summarised in the following table:

χι	Strong field (Low spin) complexes $\Delta_0 > P$			Weak field (High spin) complexes $\Delta_0 < P$			Common
d ions	Config- uration	1		Config- uration		Spin	examples
$d^1$	$t_{2g}^1$ . $e_g^0$	1	1/2	$t_{2g}^1 e_g^0$	1	1/2	Ti <sup>3+</sup>
$d^1$ $d^2$	$\begin{array}{c} t_{2g}^{1}.e_{g}^{0} \\ t_{2g}^{2}.e_{g}^{0} \end{array}$	2	1	$t_{2g}^2 e_g^0$	2	1	V <sup>3+</sup>
$d^3$ .	$t_{2g}^3 e_g^0$	3	3/2	$t_{2g}^3 e_g^0$	3	3/2	Ti <sup>3+</sup> V <sup>3+</sup> Cr <sup>3+</sup>
$d^4$	$\begin{array}{cccc} t_{2g}^4 & e_g^0 \\ t_{2g}^5 & e_g^0 \\ t_{2g}^6 & e_g^0 \end{array}$	2 .	1	$t_{2g}^3 e_g^1$	4	2	Mn <sup>3+</sup>
$d^5$	$t_{2g}^5$ , $e_g^0$	1 .	1/2	$t_{2g}^3 e_g^2$	5	5/2	Mn <sup>2+</sup> ,Fe <sup>3+</sup>
$d^6$	$t_{2g}^6 e_g^0$	0	0	$t_{2g}^4 e_g^2$	4	2	Fe <sup>2+</sup> ,Co <sup>3+</sup>
$d^7$	$t_{2g}^6 e_g^1$	1	1/2	$t_{2g}^5 e_g^2$	3	3/2	Co <sup>2+</sup>
$d^8$		2	1	$t_{2g}^6 e_g^2$	2	1	Ni <sup>2+</sup>
$d^9$	$\begin{array}{c cccc} & t_{2g}^6 & e_g^2 \\ & t_{2g}^6 & e_g^3 \end{array}$	1	1/2	$t_{2g}^6 e_g^3$	1	1/2	Cu <sup>2+</sup> Zn <sup>2+</sup>
$d^{10}$	$t_{2g}^6 e_g^4$	0	0	$t_{2g}^6 e_g^4$	0	0	Zn <sup>2+</sup>

The following conclusions are derived from the table:

(i) The distribution of electrons of  $d^1$ ,  $d^2$ ,  $d^3$ ,  $d^8$ ,  $d^9$  and  $d^{10}$  in  $t_{2g}$  and  $e_g$  sets for both strong and weak octahedral ligands fields is the same.

- (ii) For each of  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  there is difference in the arrangement of electrons in weak and strong ligands field.
- (iii) Weak field complexes of  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  ions have greater number of unpaired electrons than those of strong field complexes and thus, the resultant spins of weak field complexes have higher value than strong field complexes.

Hence, the complexes of weak field ligands are called **high** spin complexes and the complexes of strong field ligands are called **low spin complexes**.

### Calculation of CFSE

Each electron occupying  $t_{2g}$  orbital results in lowering of energy by  $-0.40~\Delta_0$  (or  $-4~\mathrm{Dq}$ ). Similarly, each electron occupying  $e_g$  orbital results in increase of energy by  $+0.60~\Delta_0$  (or  $+6~\mathrm{Dq}$ ). Thus,

CFSE = 
$$(-0.4x + 0.6y) \Delta_0$$

where, x = number of electrons occupying  $t_{2g}$  orbitals and y = number of electrons occupying  $e_g$  orbitals. Negative value of CFSE indicates net lowering in energy, i.e., gain in stability.

Calculation of CFSE Values for  $d^1$  to  $d^{10}$ Configurations

Metal ion Confi- guration	Low spin state (strong ligand field)	CFSE (Δ <sub>o</sub> )	High spin state (weak ligand field)	CFSE (Δ <sub>0</sub> )
$d^1$	$t_{2g}^1 e_g^0$	$-0.4 \times 1$ = -0.4 or -4 Dq	$t_{2g}^1 e_g^0$	$-0.4 \times 1$ = -0.4 or -4 Dq
$d^2$	$t_{2g}^2 e_g^0$	$-0.4 \times 2$ = -0.8 or -8 Dq	$t_{2g}^2 e_g^0$	$-0.4 \times 2$ = -0.8 or -8 Dq
$d^3$	$t_{2g}^3 e_g^0$	-0.4 × 3	$t_{2g}^3 e_g^0$	-0.4 × 3
$d^4$	$t_{2g}^4 e_g^0$	= -1.2  or  -12  Dq $-0.4 \times 4$	$t_{2g}^3 e_g^1$	= -1.2  or  -12  Dq $-0.4 \times 3 + 0.6$
$d^5$	$t_{2g}^5 e_g^0$	= -1.6  or  -16  Dq $-0.4 \times 5$	$t_{2g}^3 e_g^2$	= -0.6 or 6 Dq $-0.4 \times 3 + 2 \times 0.6$
d 6	$t_{2g}^6 e_g^0$	= -2.0  or  -20  Dq $-0.4 \times 6$	$t_{2g}^4 e_g^2$	$= 0.0 \text{ or } 0 \text{ Dq}$ $-0.4 \times 4 + 2 \times 0.6$
$d^{7}$	$t_{2g}^6 e_g^1$	= -2.4  or  -24  Dq $-0.4 \times 6 + 0.6$	$t_{2g}^5 e_g^2$	= -0.4 or 4 Dq $-0.4 \times 5 + 2 \times 0.6$
$d^8$	$t_{2g}^6 e_g^2$ .	$= -1.8 \text{ or } -18 \text{ Dq}$ $-0.4 \times 6 + 2 \times 0.6$	$t_{2g}^6 e_g^2$	= -0.8 or 8 Dq $-0.4 \times 6 + 2 \times 0.6$
d 9	$t_{2g}^6 e_g^3$	= -1.2  or  -12  Dq $-0.4 \times 6 + 3 \times 0.6$	$t_{2g}^{6} e_{g}^{3}$	= -1.2  or  -12  Dq $-0.4 \times 6 + 3 \times 0.6$
$d^{10}$	$t_{2g}^6 e_g^4$	$= -0.6 \text{ or } -6 \text{ Dq}$ $-0.4 \times 6 + 4 \times 0.6$ $= 0.0 \text{ or } 0 \text{ Dq}$	$t_{2g}^6 e_g^4$	= -0.6  or  -6  Dq $-0.4 \times 6 + 4 \times 0.6$ = 0.0  or  0  Dq

The above calculations show that coordination entities with four to seven *d*-electrons are more stable for strong ligand field as compared to weak ligand field.

Distribution of d-electrons in  $t_{2g}$  and  $e_g$  orbitals in tetrahedral complexes: The distribution of d-electrons in the  $t_{2g}$  and  $e_g$  sets in a tetrahedral complex in presence of weak and strong ligands field has been shown in the following table:

, X		eld (High sp omplexes	pin)	Strong field (Low spin) complexes			
d ions	Config- uration	No. of unpaired electrons	Spin	Config- uration	No. of unpaired electrons	Spin	
$d^{1}$	$t_{2g}^0 e_g^1$	. 1	1/2	$t_{2g}^0 e_g^1$	1	1/2	
$\frac{d^1}{d^2}$	$\begin{array}{cccc} t_{2g}^{0} & e_{g}^{1} \\ t_{2g}^{0} & e_{g}^{2} \end{array}$	2	1	$\begin{array}{ccc} t_{2g}^{0} & e_{g}^{1} \\ t_{2g}^{0} & e_{g}^{2} \end{array}$	2	1	
$d^3$ $d^4$	$t_{2g}^{1} e_{g}^{2}$	3	$1\frac{1}{2}$	$t_{2g}^{0} e_{g}^{3}$	1	1/2	
$d^{4}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4	2	$-t_{2g}^{0} e_{g}^{4}$	0	0	
$-d^5$	$=t_{2g}^{3}-e_{g}^{2}$	55	$\frac{1}{2}$	$t_{2g}^1$ $e_g^4$		1/2	
$d^6$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	. 4	2	$t_{2g}^2 e_g^4$	2	. 1	
$\frac{d^7}{d^8}$	$t_{2g}^3$ $e_g^4$	3.	$1\frac{1}{2}$	$t_{2g}^3 e_g^4$	3	$1\frac{1}{2}$	
$d^8$	$t_{2p}^{4} e_{p}^{4}$	2	1	$t_{2g}^4 e_g^4$	2	1	
<b>d</b>	$t_{2g}^{5}.e_{g}^{4}$	11	1/2	$t_{2g}^{5} e_{g}^{4}$	11	1/2	
$d^{10}$	$t_{2g}^{5} e_{g}^{4}$ $t_{2g}^{6} e_{g}^{4}$	0	0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0	0	

Magnetic nature: The transition metal complexes containing one or more unpaired electrons possess a definite value of magnetic moment. An unpaired electron because of its spin is equivalent to an electric current flowing in a circular conductor. Hence, it behaves as a magnet.

[The magnetic moment is expressed as :

$$\mu = \frac{eh}{4\pi mc} = 9.274 \times 10^{-21} \text{ erg gauss}^{-1}$$
= one Bohr Magneton (B.M.)

where, e = charge on electron; m = mass of electron;

h = Planck's constant; c = velocity of light

The substances having magnetic moments are attracted in external magnetic field. Such substances are termed paramagnetic substances. Most of the coordination compounds are paramagnetic. The substances having no unpaired electron or having only paired electrons show zero magnetic moment and are called diamagnetic substances.

The magnetic nature or magnetic moment of a coordination compound, thus, depends on the number of unpaired electrons. The magnetic moment is approximately given by the relation,

Magnetic moment,  $\mu = \sqrt{n(n+2)}$  B.M., where n is the number of unpaired electrons. This relationship is used to calculate the number of unpaired electrons in a complex ion. The values of n calculated by applying the above formula for different magnetic moments are given in the following table:

Magnetic moment (B.M.)	Number of unpaired electrons
1.73	1
2.83	2
3.87	3
4.90	4 .
5.92	5

The actual number of unpaired electrons in a complex can be found by magnetic measurements and in general, experimental findings support predictions based on crystal field splitting. However, a distinction between low and high spin complexes can be made only if the metal ion contains more than three and less than eight d-electrons. The high spin complex,  $[Fe(H_2O)_6]^{2+}$  has four unpaired electrons and is **paramagnetic** whereas the low spin complex,  $[Fe(CN)_6]^{4-}$  has no unpaired electrons and is **diamagnetic**.

Colour: A substance appears coloured because it absorbs light at specific wavelengths in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmits or reflects the rest of the wavelength. Each wavelength of visible light represents a different colour. White light, such as sunlight, is a combination of all colours; an object that absorbs all visible light appears black. The following table shows the relationship of wavelength absorbed to observed colour.

When the energy of the photon (hv) is equal to the difference between the lower and higher d-orbital energy levels, an electron is promoted from a lower to higher level. If the wavelength of the photon absorbed by an ion lies outside the visible region, then the transmitted light looks the same as the incident light white and the ion appears colourless.

Spectroscopic analysis offers the best means of measuring crystal field splitting. The  $[Ti(H_2O)_6]^{3+}$  ion provides a simple example, because  $Ti^{3+}$  has only one 3 *d*-electron.  $[Ti(H_2O)_6]^{3+}$  ion absorbs light in the visible region. The wavelength corresponding to maximum absorption is 498 nm. This enables us to calculate the crystal field splitting.

$$\Delta = hv = h \times \frac{c}{\lambda}$$
where  $h = \text{Planck's constant} = 6.63 \times 10^{-34} \text{ Js}$ 
and  $c = \text{velocity of light} = 3.00 \times 10^8 \text{ ms}^{-1}$ 

$$= \frac{(6.63 \times 10^{-34}) \times (3.00 \times 10^8)}{498 \times 10^{-9}}$$

$$= 3.99 \times 10^{-19} \text{ J}$$

This is the energy for one ion to excite. Thus, the energy required for one mole of ions,

$$\Delta = 3.99 \times 10^{-19} \times 6.02 \times 10^{23}$$
  
= 240,000 J mol<sup>-1</sup> = 240 kJ mol<sup>-1</sup>

Photon of energy 
$$hv$$
  $d_{x^2-y^2}$   $d_{z^2}$   $d_{z^2-y^2}$   $d_{z^2}$ 

Experiments with coordination complexes have revealed that for a given metal ion, some ligands cause a small energy separation of the *d*-orbitals, whereas others cause a large separation, *i.e.*, different ligands may bring different colours to the complex ions of the same metal ion. For example, the data for several cobalt, (III) complexes are presented in the following table:

The colours of some complexes of Co<sup>3+</sup> ion

Complex ion	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of complex observed
$[Co(F)_6]^{3-}$	700	Red	Green
$[Co(C_2O_4)_3]^{3-}$	600	Yellow	Dark green
$[Co(H_2O)_6]^{3+}$	600	Yellow	Blue-green
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow-orange
$[Co(en)_3]^{3+}$	470.	Blue	Yellow-orange
$\left[\text{Co}(\text{CN})_6\right]^{3-}$	310	Ultraviolet	Pale-yellow

The absorption maxima among the listed complexes ranges from 700 nm for  $[\mathrm{CoF}_6]^{3-}$  to 310 nm for  $[\mathrm{Co}(\mathrm{CN})_6]^{3-}$ . The ligands change from member to member in the series and is concluded that the energy of light absorbed by the complex is related to different crystal field splitting,  $\Delta_0$ , caused by different ligands. Fluoride ion causes the smallest splitting of the d-orbitals among the complexes listed, whereas cyanide caused the largest splitting.

Spectra of complexes of other metals provide similar results. This supports the spectrochemical series. The ability of crystal field theory to explain differences in the colour of transition metal complexes is one of the strengths of this theory.

# 15.7 STABILITY OF COORDINATION COMPOUNDS IN SOLUTIONS

A coordination compound is formed in solution by the stepwise addition of ligands to a metal ion. Thus, the formation of the complex,  $ML_n$  (M = central metal cation, L = monodentate ligand and n = coordination number of metal ion) may be supposed to take place by the following n consecutive steps.

$$M + L \Longrightarrow ML$$

$$K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \Longrightarrow ML_2$$

$$K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \Longrightarrow ML_3$$

$$K_3 = \frac{[ML_3]}{[ML_2][L]}$$
...
...
$$ML_{n-1} + L \Longrightarrow ML_n$$

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

 $K_1, K_2, K_3, \ldots, K_n$  are called stepwise stability constants. With a few exceptions, the values of successive stability constants decrease regularly from  $K_1$  to  $K_n$ .

The overall stability constant, K, is given as:

$$M + nL \implies ML_n$$

$$K = K_1, K_2, K_3, \ldots, K_n = \frac{[ML_n]}{[M][L]^n}$$

The higher the overall stability constant value of the complex, the more stable it is. Alternatively, 1/K values called **instability constant** explain the dissociation of the complex into metal ion and ligands in the solution.

The values of stability constants for some of the complexes are given below:

Complex	Stability constant
$[Cu(NH_3)_4]^{2+}$	$4.5\times10^{11}$
$[Ag(NH_3)_2]^+$	$1.6 \times 10^7$
$[Co(NH_3)_6]^{2+}$	$1.12\times10^6$
$[Co(NH_3)_6]^{3+}$	$5.0\times10^{33}$
[AgCl <sub>2</sub> ]	$1.11\times10^5$
[AgBr <sub>2</sub> ]	$1.28 \times 10^{7}$
$[Ag(CN)_2]^-$	$1.0 \times 10^{22}$
$\left[\mathrm{Cu}(\mathrm{CN})_4\right]^{2-}$	$2.0 \times 10^{27}$
$[Fe(CN)_6]^{3-}$	$7.69 \times 10^{43}$

From the above values, some conclusions are drawn:

(i) The values of stability constants differ widely depending on the nature of the metal ion and the ligand. In general, higher the charge density on the central ion, the greater is the stability of its complexes, *i.e.*, the higher value of

charge radius of the ion, the greater is the stability of its complexes. Electronegativity of the central ion influences the

stability. The higher the electronegativity of the central ion, the greater is the stability of its complexes.

The more basic a ligand, the greater is the ease with which it can donate its lone pairs of electrons and therefore, the greater is the stability of the complexes formed by it.

- (ii) The higher the oxidation state of the metal, the more stable is the complex. The charge density of  $\operatorname{Co}^{3+}$  ion is more than  $\operatorname{Co}^{2+}$  ion and thus,  $[\operatorname{Co}(\operatorname{NH}_3)_6]^{3+}$  is more stable than  $[\operatorname{Co}(\operatorname{NH}_3)_6]^{2+}$ . Similarly,  $[\operatorname{Fe}(\operatorname{CN})_6]^{3-}$  is more stable than  $[\operatorname{Fe}(\operatorname{CN})_6]^{4-}$ .
- (iii) The cyano and ammine complexes are far more stable than those formed by halide ions. This is due to the fact that  $NH_3$  and  $CN^-$  are strong Lewis bases.
- (iv) The complexes of bivalent cations  $(M^{2+})$  of 3*d*-series show the following order of stability:

	*			-	
Cation	Mn <sup>2+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>
Ionic size	0.91	0.83	0.82	0.78	0.69
			decrease	s	
Stability of the complex			increase	S	
		(Irving	William	order)	<del></del>

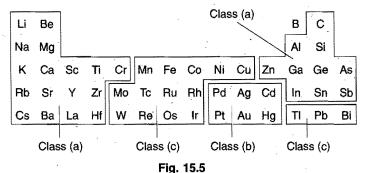
(v) Chelating ligands form more stable complexes as compared to monodentate ligands. Greater is the chelation, more is the stability of complex.

$$[Cr(NH_3)_6]^{3+}$$
 <  $[Cr(en)(NH_3)_4]^{3+}$  <  $[Cr(en)_2(NH_3)_2]^{3+}$  <  $[Cr(en)_3]^{3+}$ 

(vi) Thermodynamic stabilities of the complexes formed by various metals follow some regular trends, such as those involving size and charge effects, factors that determine the Lewis acid strength of a metal ion.

Generally, the stabilities of complexes decrease with increasing atomic number for the electropositive metals *e.g.*, group IIA or hard Lewis acids and increase with increasing atomic number for the noble metals (soft acids), following the general trend of ionization energy.

- (a) For the electropositive metals (hard acids) the order of stabilities of halide complexes is F > Cl > Br > I but for highly polarizing soft acid metal ions such as  $Hg^{2+}$ , we see reverse order.
- (b) The most electropositive metals (hardest acids) show a greater tendency for forming complexes with hard ligands such as F or oxygen containing ligands.



Metals are classified according to their acceptor properties.

Class (a)  $\longrightarrow$  **Hard acids :** Show affinities for the ligands whose basicity is proportional to protons.

Class (b) — Soft acids: form stable olefin complexes

Class (c)  $\longrightarrow$  Border line metals.

# 15.8 PREPARATION OF COORDINATION COMPOUNDS

Coordination compounds are generally prepared by the application of the following methods:

1. Ligand substitution reactions: A reaction involving the replacement of the ligands attached to the central metal ion in the complex by other ligands is called a ligand substitution reaction. Transition metal ions in aqueous solution form complex ions by bonding with water molecules. These water molecules are then replaced by ligands to form the desired complex.

$$\begin{aligned} & [\text{Cu}(\text{H}_2\text{O})_4]^{2+}(aq.) + 4\text{NH}_3(aq.) \rightarrow & [\text{Cu}(\text{NH}_3)_4]^{2+}(aq.) + 4\text{H}_2\text{O}(l) \\ & \text{(Light blue)} \end{aligned}$$

$$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}(aq.) + 6\text{NH}_3(aq.) \rightarrow [\text{Ni}(\text{NH}_3)_6]^{2+}(aq.) + 6\text{H}_2\text{O}(l)$$
(Green) (Blue-violet)

$$[\text{Ni}(\text{NH}_3)_6]^{2+}(aq.)+4\text{CN}^-(aq.)\rightarrow [\text{Ni}(\text{CN})_4]^{2-}(aq.)+6\text{NH}_3(aq.)$$
(Yellow)

- *i.e.*, tetraamminecopper sulphate, [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>, is formed by addition of ammonia solution to copper sulphate solution and potassium tetracyanonickelate(II) is obtained by the addition of potassium cyanide solution to hexaamminenickel(II) sulphate solution.
- **2. Direct mixing of reagent:** Dichloro *bis* (ethylenediamine) platinum(II) is prepared by adding platinum chloride (PtCl<sub>2</sub>) to ethylenediamine.

$$PtCl2 + 2H2N - CH2 - CH2 - NH2 - M2 - Pt(en)2Cl2$$
(en)

Similarly, hexaamminenickel(II) chloride is obtained by direct reaction between solid nickel chloride (NiCl<sub>2</sub>) and liquid ammonia.

$$NiCl_2 + 6NH_3(l) \longrightarrow [Ni(NH_3)_6]Cl_2$$

3. Redox reactions: In these reactions, either oxidation or reduction is involved. Cobalt(II) nitrate reacts with aqueous ammonium nitrate and aqueous ammonia in presence of  $H_2O_2$  (oxidising agent) to form pentaamminenitrocobalt(III) nitrate.

$$2\text{Co(NO}_3)_2 + 8\text{NH}_3 + 2\text{NH}_4\text{NO}_3 + \text{H}_2\text{O}_2 \longrightarrow$$
  
 $2[\text{Co(NH}_3)_5\text{NO}_2](\text{NO}_3)_2 + 2\text{H}_2\text{O}_3$ 

# 15.9 IMPORTANCE OF COORDINATION COMPOUNDS

The complexes are of immense importance on account of their applications in various fields. During complex formation there are drastic changes in the properties of metal atom or ion and these changes in properties are made use of in the applications of metal complexes.

## 1. Analytical chemistry

Coordination compounds find their applications in both qualitative and quantitative methods of analysis.

(a) The separation of Ag<sup>+</sup> from Hg<sub>2</sub><sup>2+</sup> in the first group of analysis is based on the fact that while silver chloride is soluble in aqueous ammonia and Hg<sub>2</sub>Cl<sub>2</sub> forms a black insoluble material.

$$\begin{array}{c} AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O \\ \\ Soluble \\ Hg_2Cl_2 + NH_4OH \longrightarrow \underbrace{Hg(NH_2)Cl + Hg + HCl + H_2O}_{Pl_1+Pl_2} \end{array}$$

(b) The separation of II B group sulphides from II A group sulphides is based on the fact that sulphides of II B group form complex sulphides with yellow ammonium sulphide which are soluble while sulphides of II A group do not react.

$$Sb_2S_5 + 3(NH_4)_2S \longrightarrow 2(NH_4)_3[SbS_4]$$

$$As_2S_5 + 3(NH_4)_2S \longrightarrow 2(NH_4)_3[AsS_4]$$

$$SnS_2 + (NH_4)_2S \longrightarrow (NH_4)_2[SnS_3]$$

(c) The detection of Cu<sup>2+</sup> is based on the formation of a blue tetraammine copper sulphate complex which gives a deep blue coloured solution.

$$CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$$

It also forms a chocolate coloured precipitate with potassium ferrocyanide.

$$2CuSO_4 + K_4Fe(CN)_6 \longrightarrow Cu_2[Fe(CN)_6] + 2K_2SO_4$$
Chocolate ppt.

(d) Fe<sup>3+</sup> is detected by formation of a blood red coloured complex with KSCN.

$$Fe^{3+} + KSCN \longrightarrow [Fe(SCN)]^{2+} + K^{+}$$
Blood red colour

(e) The detection and estimation of Ni<sup>2+</sup> is based on the formation of a scarlet red complex with dimethyl glyoxime.

$$CH_{3}-C=NOH$$

$$NiCl_{2}+2 \qquad | \qquad +2NH_{4}OH \longrightarrow$$

$$CH_{3}-C=NOH$$

$$OH \qquad 0$$

$$CH_{3}-C=N \qquad N=C-CH_{3}$$

$$CH_{3}-C=N \qquad N=C-CH_{3}$$

$$CH_{3}-C=N \qquad N=C-CH_{3}$$

$$O \qquad OH$$

Scarlet red precipitate

(f) Many ligands (organic reagents) are used for the gravimetric estimation of a number of metal ions.

Metal ion to be estimated	Organic reagent used
Cu <sup>2+</sup>	Benzoin oxime
Ni <sup>2+</sup>	Dimethyl glyoxime
Fe <sup>3+</sup>	1, 10-phenanthroline
A1 <sup>3+.</sup>	8-hydroxyquinoline
Co <sup>2+</sup>	α-nitroso β-naphthol

- (g) EDTA is used as a complexing agent in volumetric analysis of metal ions like Ca<sup>2+</sup>, Mg<sup>2+</sup> and Zn<sup>2+</sup>.
- (h) The coordination compounds of the transition metals exhibit a variety of colours. This property is utilised in colorimetric analysis for the estimation of many metals.
- (i) Other analytical applications of coordination compounds are oxidation-reduction indicators, estimation of hardness in water, sequestering reagents and solvent extraction.

### 2. Metallurgical operations

Silver and gold are extracted by the use of complex formation. Silver ore is treated with sodium cyanide solution with continuous passing of air through solution. Silver dissolves as a cyanide complex and pure silver is precipitated by the addition of scrap zinc.

$$Ag_2S + 4NaCN \implies 2Na[Ag(CN)_2] + Na_2S$$

$$4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$$

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

Native Ag and Au also dissolve in NaCN solution in presence of oxygen of the air.

$$4 Ag + 8 NaCN + O_2 + 2 H_2O \longrightarrow 4 Na[Ag(CN)_2] + 4 NaOH$$

Ag and Au are precipitated by addition of scrap zinc.

Nickel is extracted by converting it into a volatile complex, nickel carbonyl by use of carbon monoxide (Mond's process). The complex decomposes on heating again into nickel and carbon monoxide.

$$Ni + 4CO \longrightarrow Ni(CO)_4 \xrightarrow{Heating} Ni + 4CO$$
(Associated with other metals)

# 3. Photography

In photography, the image on the negative is fixed by dissolving all the remaining silver halides with hypo solution in the form of a soluble complex.

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$
(Soluble) (Soluble)

## 4. Electroplating

Metal complexes release metal slowly and thus give a uniform coating in electroplating of the metal on the desired object. Cyano complexes of silver, gold, copper, etc., are used for the electrodeposition of these metals.

### 5. Biological processes

Coordination compounds play many important roles in animals and plants. They are essential in storage and transport of oxygen, as electron transfer agents, as catalysts and in photosynthesis. Three important examples are given below:

(i) Haemoglobin: Haemoglobin is a protein which is present in blood. The main function of haemoglobin is to carry oxygen in the blood from the lungs to the tissues where it

delivers the oxygen molecules to myoglobin. The quadridentate macrocyclic ligand, the porphine molecule is an important

part of haemoglobin structure. The two H<sup>+</sup> ions bonded to nitrogen atoms are displaced and the metal ion coordinate simultaneously with all the four nitrogen atoms. The complex formed from porphine is called **porphyrin**. The Fe-complex is called heme. Haemoglobin molecule consists four heme groups embedded in a protein molecule. The iron in the heme group has the oxidation number +2. It is coordinated to the four nitrogen donor atoms in the porphine group and also, to a nitrogen donor atom in a ligand group which is attached to the protein. The sixth ligand is a water molecule, which binds to the Fe<sup>2+</sup> ion on the other side of the ring to complete the octahedral complex. Under these conditions, the haemoglobin molecule is called deoxyhaemoglobin and has a blue colour. The water ligand can be replaced readily by molecular oxygen to form red coloured oxyhaemoglobin. This haemoglobin flows from lungs to tissues where it is again deoxygenated.

The iron-heme complex is present in another class of proteins, called **cytochromes**. Cytochromes act as electron carriers which also play an essential part in metabolic processes.

Oxy-haemoglobin

In cytochromes iron undergoes rapid reversible redox reactions.

$$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$$

(ii) Chlorophyll: The chlorophyll molecule, which plays an essential role in photosynthesis also contains the porphyrin ring but the metal ion there is Mg<sup>2+</sup> rather than Fe<sup>2+</sup>. It is a green plant pigment and acts as a photosensitizer in the synthesis of carbohydrates in plants. It is structurally similar to heme.

$$6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{hv} \text{Chlorophyll} C_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$$

$$CH_{2}$$
 $CH_{3}$ 
 $CH_{3}$ 
 $CH_{3}$ 
 $CH_{2}$ 
 $CH_{3}$ 
 $CH_{2}$ 
 $CH_{3}$ 
 $CH_{2}$ 
 $CH_{3}$ 
 $CH_{2}$ 
 $CH_{3}$ 
 $CH_{2}$ 
 $COOC_{20}$ 
 $COOC_{20}$ 
 $COOC_{20}$ 
 $COOC_{20}$ 

Structure of Chlorophyll

A molecule of chlorophyll can add one or two molecules of water axially. These coordinated water molecules through hydrogen bonding help the other chlorophyll molecules to associate with each other.

(iii) Vitamin  $B_{12}$ : It is a complex of cobalt with a quadridentate ligand which is similar to porphyrin ligand of haemoglobin. It has been observed that vitamin  $B_{12}$  is active only when cobalt is present in +1 oxidation state. It is a red crystalline substance which is slightly soluble in water. It is not found in plants but is found in all animal tissues. It is present mainly in milk, eggs, cheese and meat.

It is essential growth factor for many microorganisms.

### 6. Plant growth

Plants require a number of nutrients for healthy growth. Essential nutrients include a number of metals such as Fe, Zn, Cu, Mn, Mo, etc. For example, the deficiency of iron brings a disorder in plants known as **iron chlorosis**. This disorder affects the yield of fruit from citrus trees. Iron in +3 state present in the soil is mostly hydrolysed to form insoluble iron hydroxide Fe(OH)<sub>3</sub>, which cannot be taken up by plants. To overcome iron deficiency, the complex Fe(III)–EDTA is added to the soil. This complex is soluble in water and readily enters the roots of trees and reach to various parts of the plants where it is converted into useful compounds.

### 7. In medicinal field

- (i) The complex of calcium with EDTA is used for the treatment of lead poisoning. Lead readily replaces calcium in the complex and lead-EDTA complex is finally eliminated from the body in urine.
- (ii) The platinum complex cis [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] known as cis-platin is used as an antitumor agent in the treatment of cancer.

### 15.10 ORGANOMETALLIC COMPOUNDS

Compounds that contain at least one carbon-metal bond are called organometallic compounds. Zeise, in 1830, prepared the first organometallic compound by the action of ethylene on a solution of potassium chloroplatinate(II). In the last four decades, enormous work has been done in this field and many fascinating compounds have been synthesised and investigated. Grignard reagent, RMgX is a familiar example of organometallic compounds where R is an alkyl group. Diethyl zinc [Zn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>], lead tetraethyl [Pb(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>], ferrocene [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>], dibenzene chromium [Cr(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>], metal carbonyls are other examples of organometallic compounds. The compounds of metalloids such as germanium and antimony and non-metallic elements such as boron and silicon are also included under this classification.

Organometallic compounds may be classified in three classes:

- 1. Sigma (σ) bonded complexes,
- 2. Pi  $(\pi)$  bonded complexes,
- 3. Complexes containing both  $\sigma$  and  $\pi$ -bonding characteristics.

## 1. Sigma bonded complexes

In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond, *i.e.*, the ligand contributes one electron and is, therefore, called one electron donor. Examples are:

- (i) Grignard reagent, R—Mg—X where R is an alkyl or aryl group and X is a halogen.
- (ii) Zinc compounds of the formula  $R_2$ Zn such as  $(C_2H_5)_2$ Zn. This was first isolated by Frankland in 1849. Other similar compounds are  $(CH_3)_4$ Sn,  $(C_2H_5)_4$ Pb,  $Al_2(CH_3)_6$ ,  $Al_2(C_2H_5)_6$  and  $Pb(CH_3)_4$ , etc.

Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> is a dimeric compound and has a structure similar to diborane, B<sub>2</sub>H<sub>6</sub>. It is an electron deficient compound and two methyl groups act as bridges between two aluminium atoms.

# **2.** $\pi$ -bonded organometallic compounds

These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond that involves the  $\pi$  electrons of the ligand. Three common examples are Zeise's salt, ferrocene and dibenzene chromium. These are shown here:

Zeise's salts Fe  $K[PtCl_3(\eta^2-C_2H_4)]$  Fe $(\eta^5$ 

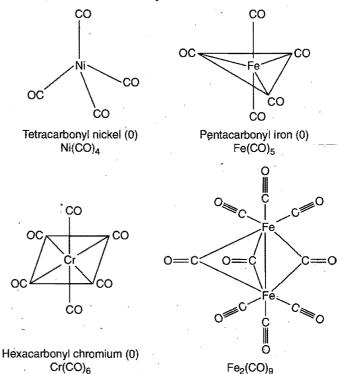
Ferrocene Dibenzene chromium  $Fe(\eta^5 - C_5H_5)_2$   $Cr(\eta^6 - C_6H_6)_2$ 

The number of carbon atoms bound to the metal in these compounds is indicated by the Greek letter ' $\eta$ ' (eta) with a number. The prefixes  $\eta^2$ ,  $\eta^5$  and  $\eta^6$  indicate that 2, 5 and 6 carbon atoms are bound to the metal in the compound.

# **3.** σ- and $\pi$ -bonded organometallic compounds

Metal carbonyls, compounds formed between metal and carbon monoxide belong to this class. These compounds possess both  $\sigma$ - and  $\pi$ - bonding. The oxidation state of metal atoms in these compounds is zero. Carbonyls may be monomeric, bridged or polynuclear. Carbonyls are mainly formed by the transition metals of VIth, VIIth and VIIIth groups.

Some well known examples are:



In a metal carbonyl, the metal-carbon bond possesses both the  $\sigma$ - and  $\pi$ -character. A  $\sigma$ -bond between metal and carbon atom is formed when a vacant hybrid bond of the metal atom overlaps with an orbital on C atom of carbon monoxide containing a lone pair of electrons.

$$\bigcirc M + + + \bigcirc C =: \longrightarrow \bigcirc M \bigcirc C = 0:$$

Formation of  $\pi$ -bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding  $\pi^*$  orbital of C atom of carbon monoxide. This overlap is also called back donation of electrons by metal atom to carbon. It has been shown below:

The  $\pi$ -overlap is perpendicular to the nodal plane of  $\sigma$ -bond.

In olefinic complexes, the bonding  $\pi$ -orbital electrons are donated to the empty orbital of the metal atom and at the same time back bonding occurs from filled orbital of the metal atom to the antibonding  $\pi$ -orbital of the olefin.

## Preparation of organometallic compounds

The following methods are generally employed for the preparation of organometallic compounds:

(i) Reaction between a metal and an organic halide: Alkali metal directly reacts with organic halide in ether to form organoalkali compounds.

$$2M + RX \xrightarrow{\text{Ether}} RM + MX$$

$$(M = \text{Li, Na, K})$$
 $C_4H_9\text{Br} + 2\text{Li} \longrightarrow C_4H_9\text{Li} + \text{LiBr}$ 
*n*-Butyl bromide

*n*-Butyl lithium

Grignard reagent is prepared when haloalkane in ether is allowed to stand over magnesium turnings for a few hours.

$$Mg + R - X \xrightarrow{Ether} R - Mg - X$$
Grignard reagent

(ii) By use of Grignard reagent: Tetraalkyl derivatives of silicon, germanium, tin and lead are prepared by the reaction of Grignard reagent and the metal halide. The reaction is carried in ether.

$$4\text{CH}_3\text{MgBr} + \text{PbCl}_4 \xrightarrow{\text{Ether}} (\text{CH}_3)_4\text{Pb} + 4\text{Mg(Br)Cl}$$
  
 $2\text{CH}_3\text{MgBr} + \text{CdCl}_2 \xrightarrow{\text{Ether}} (\text{CH}_3)_2\text{Cd} + 2\text{Mg(Br)Cl}$   
Similarly, organolithium compounds may be used.

$$SnCl_4 + 4C_4H_9Li \longrightarrow (C_4H_9)_4Sn + 4LiCl$$
*n*-Butyl tin

(iii)  $\pi$ -complexes such as ferrocene, Zeise's salt and dibenzene chromium are prepared by the application of following reactions:

(iv) Metal carbonyls are formed by direct carbonylation of the metal or reductive carbonylation.

Ni + 4CO 
$$\xrightarrow{80^{\circ}\text{C}}$$
 Ni(CO)<sub>4</sub>

$$OsO_4 + 9CO \xrightarrow{\text{High press.}} Os(CO)_5 + 4CO_2$$

Bridged carbonyls can be obtained by photolysis of monomeric carbonyls.

$$2Fe(CO)_5 \longrightarrow Fe_2(CO)_9 + CO$$

## Applications of organometallic compounds

The applications of organometallic compounds are numerous. Some important ones are mentioned here:

- 1. Tetraethyl Lead (TEL) is used as antiknock compound in gasoline.
  - 2. Silicones are used as polymers of unique properties.
- 3. Organoalkali and Grignard reagents are used in many organic synthetic reactions.
- 4. The extraction and purification of nickel is based on the formation of organometallic compound, Ni(CO)<sub>4</sub>.
- 5. Organometallic compounds are used as homogeneous and heterogeneous catalysts. Wilkinson's catalyst,  $[Rh(P \cdot Ph_3)_3Cl]$  is used as homogeneous catalyst in the hydrogenation of alkenes. Zeigler-Natta catalyst  $[TiCl_4]$  and triethyl aluminium] acts as a heterogeneous catalyst in the polymerisation of ethylene into polyethylene.

# **SOME SOLVED PROB**

**Example 1.** What is the coordination number of the central metal ions in the following complexes?

- (i)  $[Cu(NH_3)_4]^{2+}$
- (ii)  $[Fe(C_2O_4)_3]^{3-}$
- (iii)  $[Pt(en)_2Cl_2]$
- (iv)  $[Mo(CN)_8]^{4-}$
- (v)  $[Fe(EDTA)]^-$
- (vi)  $[Pd(H_2O)_2(ONO)_2I_2]$

### Solution:

(i) NH<sub>3</sub> is monodentate ligand.

Points of attachment with  $Cu^{2+} = 4 \times 1 = 4$ C.N. of  $Cu^{2+} = 4$ 

(ii)  $C_2O_4^{2-}$  is a bidentate ligand. Points of attachment with  $Fe^{3+} = 3 \times 2 = 6$ 

 $- C.N. \text{ of } Fe^{3+} = 6$ 

(iii) 'en' is a bidentate ligand and Cl is a monodentate ligand.

Points of attachment with  $Pt^{2+} = 2 \times 2 + 2 \times 1 = 6$ C.N. of  $Pt^{2+} = 6$ 

(iv) CN is a monodentate ligand.

Points of attachment with  $Mo^{4+} = 8 \times 1 = 8$ 

C.N. of  $Mo^{4+} = 8$ 

(v) EDTA is a hexadentate ligand.

Points of attachment with  $Fe^{3+} = 6 \times 1 = 6$ 

C.N. of  $Fe^{3+} = 6$ 

(vi) Points of attachment with

$$Pd^{4+} = 2 \times 1 + 2 \times 1 + 2 \times 1 = 6$$
  
C.N. of  $Pd^{4+} = 6$ 

Example 2. Calculate the oxidation state of the central metal atom in the following:

- (i)  $[Co(NH_3)_5Cl]^{2+}$
- (ii)  $K_4[Fe(CN)_6]$
- (iii)  $[Co(NO_2)_2(py)_2(NH_3)_2]NO_3$  (iv)  $Ni(CO)_4$
- $(v) [Fe(EDTA)]^T$

### Solution:

(i) 
$$x + 5 \times (0) - 1 = +2$$
  
 $x = +2 + 1 = 3$  Oxi. state of Co = +3

 $4 \times (+1) + x + 6 \times (-1) = 0$ (ii)

or x = +6 - 4 = +2Oxi. state of Fe = +2

 $x + 2 \times (-1) + 2 \times (0) + 2 \times (0) -1 = 0$ (iii)

or x = +2 +1 = +3Oxi. state of Co = +3

 $x + 4 \times (0) = 0$ (iv)

x = 0Oxi. state of Ni = 0

 $x + 1 \times (-4) = -1$ or x = +4 - 1 = +3Oxi. state of Fe =+3

Example 3. Give the IUPAC names of the following compounds:

- (i)  $K_3[Al(C_2O_4)_3]$
- (ii)  $[Pt(NH_3)_4(NO_2)Cl]SO_4$
- (iii)  $K_3[Cr(CN)_6]$
- (iv)  $[Co(NH_3)_5ONO]Cl_2$

 $(v) [Cr(NH_3)_5CO_3]Cl$ 

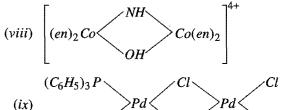
[L.I.T. 1996]

(vi)  $[Cr(NH_3)_5(NCS)][ZnCl_4]$ 

[L.I.T. 1997]

 $P(C_6H_5)_3$ 

(vii)  $KAu(CN)_2$ 



### Solution:

- (i) Potassium trioxalatoaluminate (III)
- (ii) Tetraamminechloronitrito-n-platinum (IV) sulphate
- (iii) Potassium hexacyanochromate (III)
- (iv) Pentaamminenitritito-o-cobalt (III) chloride
- (v) Pentaamminecarbonatochromium (III) chloride
- (vi) Pentaammineisothiocyanatochromium (III) tetrachlorozincate (II)
- (vii) Potassium dicyanoaurate (I)
- (viii) Bis (ethylenediamine) cobalt (III)-μ-imido-μ-hydrobis (ethylenediammine) cobalt (III) ion
- (ix) Chlorotriphenylphosphinepalladium (II)-μ-dichlorochlorotriphenylphosphinepalladium (II).

**Example 4.** Name the type of isomerism exhibited by the following isomers:

- (i)  $[Cr(NH_3)_6][Cr(CN)_6]$  and  $[Cr(NH_3)_4(CN)_2][Cr(NH_3)_2(CN)_4]$
- (ii)  $[Co(py)_2(H_2O)_2Cl_2]Cl$  and  $[Co(py)_2(H_2O)Cl_3]H_2O$
- $(iii) [Pt(NH_3)_4Br_2]Cl_2$ and  $[Pt(NH_3)_4Cl_2]Br_2$
- (iv)  $[Co(NH_3)_5NO_2]Cl_2$  and  $[Co(NH_3)_5ONO]Cl_2$

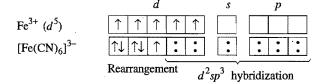
Solution: (i) Coordination isomerism

- (ii) Hydrate isomerism
- (iii) Ionisation isomerism
- (iv) Linkage isomerism

Example 5. How would you account for the following? (a)  $[Fe(CN)_6]^{3-}$  is weakly paramagnetic while  $[Fe(CN)_6]^4$ is diamagnetic.

- (b) Ni(CO)<sub>4</sub> possesses tetrahedral geometry while  $[Ni(CN)_4]^{2-}$  is square planar.
- (c)  $[Ni(CN)_4]^{2-}$  is diamagnetic while  $[NiCl_4]^{2-}$  is paramagnetic.

**Solution**: (a)  $[Fe(CN)_6]^{3-}$  involves  $d^2sp^3$  hybridization.

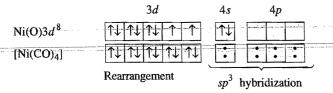


One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.

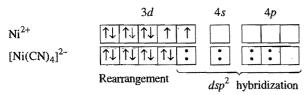
 $[Fe(\tilde{CN})_6]^{4-}$  involves also  $d^2sp^3$  hybridization but it has Fe<sup>2+</sup> ion as central ion.

All orbitals are doubly occupied, hence it is diamagnetic in nature.

(b) In the formation of Ni(CO)<sub>4</sub>, nickel undergoes sp<sup>3</sup> hybridization, hence it is tetrahedral in shape.



In the formation of [Ni(CN)<sub>4</sub>]<sup>2-</sup>, Ni<sup>2+</sup> ion undergoes dsp<sup>2</sup> hybridization, hence it is square planar in shape.



(c) In [Ni(CN)<sub>4</sub>]<sup>2-</sup> all orbitals are doubly occupied, hence it is diamagnetic while in [NiCl<sub>4</sub>]<sup>2-</sup>, two orbitals are singly occupied, hence it is paramagnetic in nature.

$$[NiCl_4]^{2-}$$

$$1 \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow$$

$$sp^3 \text{ hybridization}$$

Strong field ligands like CN, CO, en, NO<sub>2</sub> have very strong electron donating tendency, hence, electrons of central metal ion pair up against Hund's rule (low spin complex).

Example 6. A metal complex having composition  $Cr(NH_3)_4Cl_2Br$  has been isolated in two forms (A) and (B). The form (A) reacts with AgNO<sub>3</sub> to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of (A) and (B) and state the hybridization of chromium in each. Calculate the magnetic moments (spinonly value). [I.I.T. 2001]

### **Solution:**

Complex, Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>Br, has two isomers. Since, coordination number of Cr is six, the two forms may be represented in the following way:

$$\begin{array}{cccc} [\text{Cr}(\text{NH}_3)_4\text{ClBr}] & \text{Cl} & [\text{Cr}(\text{NH}_3)_4\text{Cl}_2] & \text{Br} \\ & & (\textit{B}) & & & & & & & & & & & \\ \end{array}$$

[Cr(NH<sub>3</sub>)<sub>4</sub>ClBr] Cl + AgNO<sub>3</sub> 
$$\longrightarrow$$
 [Cr(NH<sub>3</sub>)<sub>4</sub>ClBr] NO<sub>3</sub> +

(A) AgCl $\downarrow$ 

White ppt.

AgCl + 2NH<sub>4</sub>OH  $\longrightarrow$  Ag(NH<sub>3</sub>)<sub>2</sub>Cl + 2H<sub>2</sub>O

Soluble

[Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>] Br + AgNO<sub>3</sub>  $\longrightarrow$  [Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>] NO<sub>3</sub>+ AgBr $\downarrow$ 

(B) Pale yellow

(B) Pale 
$$AgBr + 2NH_4OH \longrightarrow Ag(NH_3)_2Br + 2H_2O$$
 Soluble Soluble

The state of hybridization of chromium in both the complexes is  $d^2sp^3$ . Chromium is in trivalent state (Cr<sup>3+</sup>).

As three unpaired electrons are present,

the magnetic moment 
$$=\sqrt{n(n+2)}$$
 B.M.

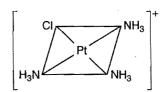
$$= \sqrt{3 \times 5}$$
 B.M. = 3.87 B.M.

Example 7. Platinum (II) forms square planar complexes and platinum (IV) gives octahedral complexes. How many geometrical isomers are possible for each of the following complexes? Describe their structures:

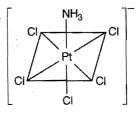
- (a)  $[Pt(NH_3)_3Cl]^+$
- (c)  $[Pt(NH_3)_2ClNO_2]$
- (b)  $[Pt(NH_3)Cl_5]^-$ (d)  $[Pt(NH_3)_4ClBr]^{2+}$

### Solution:

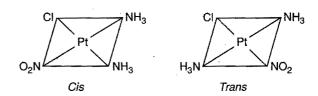
(a) No isomers are possible for a square planar complex of the type  $MA_3B$ .



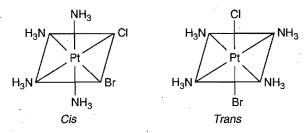
(b) No isomers are possible for an octahedral complex of the type  $MAB_5$ .



(c) Cis and trans-isomers are possible for a square planar complex of the type  $MA_2BC$ .



(d) Cis and trans-isomers are possible for an octahedral complex of the type  $MA_4BC$ .



### **Example 8.** Answer the following:

- (a) Why ligand field theory is also called crystal field theory?
  - (b) What is crystal field splitting?
  - (c) What are  $t_{2g}$  and  $e_g$  orbitals?

### **Solution:**

- (a) According to this theory, the bond between metal ion and ligands is ionic, *i.e.*, the electrostatic interactions are similar to those present in the crystals amongst the ions. That is why, the ligand field theory is also called crystal field theory.
- (b) In the free transition metal atom or ion, all the five d-orbitals are degenerate but under the influence of ligands when complex formation occurs, the d-orbitals are split into two sets of orbitals  $t_{2g}$  and  $e_g$  orbitals. This is called crystal field splitting.
- (c) Under the influence of ligands, when complex formation occurs, the five degenerate d-orbitals are split into two types of d-orbitals  $t_{2g}$  (three degenerate orbitals,  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$ ) and  $e_g$  (two degenerate orbitals,  $d_{z^2}$  and  $d_{x^2-y^2}$ ). Both sets have different energies.

In octahedral complexes,  $t_{2g}$  orbitals possess low energy in comparison to  $e_g$  orbitals while in tetrahedral complexes,  $t_{2g}$  orbitals possess high energy in comparison to  $e_g$  orbitals.

**Example 9.** Arrange the following complexes in order of increasing crystal field splitting:

$$[Fe(H_2O)_6]^{2+}$$
,  $[Fe(H_2O)_6]^{3+}$ ,  $[FeCl_6]^{4-}$  and  $[Ru(H_2O)_6]^{3+}$ 

### Solution :

The strength of the splitting depends on the ligand, the charge on the metal and the position of the metal in the periodic table

Ligand  $Cl^-$  is lower in the spectrochemical series than  $H_2O$ . Thus,  $[FeCl_6]^{4-}$  has low splitting relative to others.

In  $[FeCl_6]^{4-}$  and  $[Fe(H_2O)_6]^{2+}$  complexes, iron is in its +2 oxidation state but the metal is in +3 oxidation state in  $[Fe(H_2O)_6]^{3+}$  and  $[Ru(H_2O)_6]^{3+}$  complexes. The complexes with +3 oxidation states have larger splitting.

$${\rm [FeCl_6]}^{4-} \, < \, {\rm [Fe(H_2O)_6]}^{2+} \, < \, {\rm [Fe(H_2O)_6]}^{3+}, \ \, {\rm [Ru(H_2O)_6]}^{3+}$$

Three complexes contain iron, a metal with 3d valence electrons but the fourth contains ruthenium with 4d valence

electrons. The metal with 4d electrons has larger splitting in comparison to the metal with 3d electrons. Thus, the order of crystal field splitting in the given complexes is:

$$[FeCl_6]^{4-} < [Fe(H_2O)_6]^{2+} < [Fe(H_2O)_6]^{3+} < [Ru(H_2O)_6]^{3+}$$

**Example 10.** For each octahedral complex ion,  $[Fe(H_2O)_6]^{2+}$  and  $[Fe(CN)_6]^{4-}$ , draw an orbital splitting diagram and predict the number of unpaired electrons and the magnetic nature.

**Solution:** Fe<sup>2+</sup> has  $3d^6$  configuration. H<sub>2</sub>O is a weakfield ligand so it forms high spin complex while CN<sup>-</sup> is a strong-field ligand and forms low spin complex. The orbital splitting diagrams are shown below:

The  $[Fe(H_2O)_6]^{2+}$  has four unpaired electrons and hence, it is paramagnetic in nature. The  $[Fe(CN)_6]^{4-}$  has no unpaired electron and hence, it is diamagnetic in nature.

**Example 11.** Explain when hexacyano complexes of metals in their +2 oxidation state are usually yellow, but the corresponding hexacqua compounds are often blue or green.

### **Solution:**

The ligand,  $CN^-$  is near the top of the spectrochemical series, it generates a relatively large energy gap between the two sets of d-orbitals. The hexacyano complexes are yellow because they absorb high-energy indigo light. The corresponding aqua complexes have a much smaller crystal field splitting energy. They absorb orange or red light, thus appearing blue or green.

**Example 12.** Indicate the types of isomerism exhibited by the following complexes and draw the structures of these isomers.

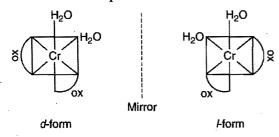
- (a)  $K[Cr(H_2O)_2(C_2O_4)_2]$
- (b)  $[Co(en)_3]Cl_3$
- (c)  $[Co(NH_3)_5NO_2](NO_3)_2$
- (d)  $[Pt(NH_3)(H_2O)Cl_2]$

### **Solution:**

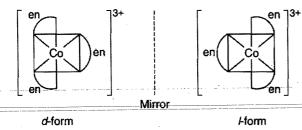
(a)  $K[Cr(H_2O)_2(C_2O_4)_2]$  shows geometrical isomerism.

$$K^{+}$$
 $\begin{bmatrix} H_{2}O \\ K^{+} \end{bmatrix}$ 
 $Cis$ -isomer
 $K^{+}$ 
 $\begin{bmatrix} H_{2}O \\ K^{+} \end{bmatrix}$ 
 $K^{+}$ 
 $\begin{bmatrix} H_{2}O \\ K^{+} \end{bmatrix}$ 
 $K^{+}$ 
 $\begin{bmatrix} H_{2}O \\ K^{+} \end{bmatrix}$ 
 $\begin{bmatrix} H_{2}O \\ K^{+} \end{bmatrix}$ 

Cis-isomer exhibits optical isomerism.



(b) [Co(en)<sub>3</sub>]Cl<sub>3</sub> exhibits optical isomerism.



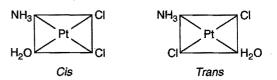
(c)  $[Co(NH_3)_5NO_2](NO_3)_2$  shows ionisation isomerism.  $[Co(NH_3)_5NO_2](NO_3)_2$ ,  $[Co(NH_3)_5NO_3](NO_2)(NO_3)$ 

This also shows linkage isomerism.

[Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>,

[Co(NH<sub>3</sub>)<sub>5</sub>(ONO)]NO<sub>3</sub>

(d) [Pt(NH<sub>3</sub>)(H<sub>2</sub>O)Cl<sub>2</sub>] shows geometrical isomerism.



**Example 13.** Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number of the central atom in the complex. Also give stereochemistry and magnetic moment of the complex.

- (i)  $K[Cr(H_2O)_2(C_2O_4)_2] \cdot 3H_2O$
- (ii) [ $Co(NH_3)_5Cl$ ] $Cl_2$
- (iii)  $CrCl_3(py)_3$
- (iv)  $Cs[FeCl_4]$
- $(v) K_4[Mn(CN)_6]$

### **Solution:**

Complex	TUPAC name	Oxidation state	Electronic configuration	Coordination number	Stereo- chemistry	Magnetic moment
(i) K[Cr(H <sub>2</sub> O) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ]·3H <sub>2</sub> O	Potassium diaquodioxalatochromate (III) hydrate	+3	3d <sup>3</sup>	6	Octahedral $d^2sp^3$ -hybridization	$\sqrt{3\times5}$ = 3.87 B.M.
(ii) [Co(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>2</sub>	Pentaamminechloridocobalt (III) chloride	+3	3d <sup>6</sup>	6	Octahedral	0
(iii) CrCl <sub>3</sub> (py) <sub>3</sub>	Trichloridotripyridinechromium (III)	+3	$3d^3$	. 6	Octahedral	$\sqrt{3 \times 5}$ = 3.87 B.M.
(iv) Cs[FeCl <sub>4</sub> ]	Caesium tetrachloridoferrate (III)	+3	3d <sup>5</sup>	4	Tetrahedral	$\sqrt{5 \times 7}$ = 5.92 B.M.
(v) K <sub>4</sub> [Mn(CN) <sub>6</sub> ]	Potassium hexacyanomanganate (II)	+2	3d <sup>5</sup>	6	Octahedral	$\sqrt{1\times3}$ = 1.73 B.M.

**Example 14.** What is meant by chelate effect? Give an example.

### **Solution:**

When a bidentate or polydentate ligand contains donor atoms in such a way that after coordinating with central metal atom forms a five or six membered ring, the effect is called 'chelate effect'.

$$\begin{bmatrix} H_2C-H_2N & NH_2-CH_2 \\ | & | & NH_2-CH_2 \end{bmatrix}^{2+}$$

$$Diethylenediamminecupric (II) ion$$

**Example 15.** What will be the correct order for the wavelengths of absorption in the visible region of the following?

 $[Ni(H_2O)_6]^{2+}, [Ni(NH_3)_6]^{2+}, [Ni(NO_2)_6]^{4-}$ 

#### Solution

In all the three complexes, the central metal ion is the same, hence, the increasing field strengths of the ligands from the spectrochemical series are in the order:

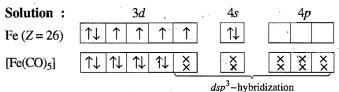
$$H_2O < NH_3 < NO_2$$

Thus, the energies absorbed for excitation will be in the order:

$$[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$$

As  $E = \frac{hc}{\lambda}$ , the wavelength absorbed will be in opposite order.

**Example 16.** Using valence bond theory explain the geometry and magnetic behaviour of pentacarbonyliron (III).



Hence, Fe(CO)<sub>5</sub> has trigonal bipyramidal geometry and as no unpaired electron is present, it is diamagnetic.

**Example 17.**  $[NiCl_4]^{2-}$  is paramagnetic while  $Ni(CO)_4$  is diamagnetic though both are tetrahedral. Why?

### Solution:

In Ni(CO)<sub>4</sub>, the oxidation state of nickel is zero and CO is a strong ligand. Due to strong ligand field, the unpaired electrons of 3*d*-orbitals get paired by 4*s*-electrons.

In [NiCl<sub>4</sub>]<sup>2-</sup>, the oxidation state of nickel is +2 and Cl<sup>-</sup> is a weak ligand. Due to weak ligand field, there is no regrouping of electrons.

**Example 18.** Draw crystal field energy level diagrams and predict the number of unpaired electrons for the following complexes:

- (a)  $[FeCl_4]^-$  (tetrahedral)
- (b)  $[NiCl_4]^{2-}$  (tetrahedral)
- (c)  $[Cr(en)_3]^{3+}$  (octahedral)

### **Solution:**

(a)	(b)	(c)
Cl is weak field	Cl is a weak field	(en) is a strong field
ligand. Thus, the	ligand. Thus, the	ligand. The electrons
complex is high spin.	complex is high spin.	occupy the orbitals
All the five orbitals	$Ni^{2+}(3d^8)$	of lower energy.
are singly occupied.		$\operatorname{Cr}^{3+}(3d^3)$
$\uparrow$ $\uparrow$ $\uparrow$	$\uparrow \downarrow \uparrow \uparrow$	
<u> </u>	1 1	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$
No. of unpaired		
electrons $= 5$	electrons = 2	electrons = 3

**Example 19.** Explain why nearly all tetrahedral complexes are high spin?

### Solution:

Because none of the orbitals point directly at the ligands in tetrahedral geometry and there are only four ligands instead of six (as in octahedral geometry), the crystal field splitting in tetrahedral complexes is only about half of that in octahedral complexes. Consequently,  $\Delta$  is almost always smaller than spin-pairing energy P, and nearly all tetrahedral complexes are high spin.

**Example 20.** Why are metals complexed in biological systems?

### **Solution:**

There are two main reasons. These are:

- (i) Uncomplexed metal ions, e.g., Fe(III) may not dissolve in water at physiological pH.
- (ii) Uncomplexed metal ions may not have the required oxidation state. For example, in vitamin  $B_{12}$ , cobalt has +1 oxidation state which is not stable when uncomplexed.

**Example 21.** Name two coordination compounds which are biologically important.

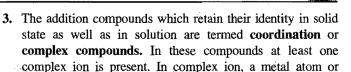
### **Solution:**

dination.

- (i) Haemoglobin—an iron complex—the red pigment in the blood that transports oxygen.
- (ii) Chlorophyll—a magnesium complex—a green pigment in plants acts as a catalyst (photosensitizer) in the synthesis of carbohydrates.

# Ö

# SUMMARY AND IMPORTANT POINTS TO REMEMBER



ion is surrounded by a number of groups through coor-

compounds, and (ii) Coordination or complex compounds.

2. The addition compounds which are stable in solid state but are broken down into individual constituents when dissolved in water are called **double salts.** Mohr's salt, potash alum,

carnallite, etc., are some examples of double salts.

1. When solutions of two or more simple stable compounds in

molecular proportions are allowed to evaporate, crystals of

new compounds may be formed. These compounds are

termed molecular or addition compounds. Addition com-

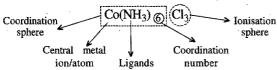
pounds are of two types: (i) Double salts or lattice

4. Complex compounds are mainly formed by transition metals but to a small extent by other metals such as magnesium in chlorophyll. Transition metals form complexes due to the given reasons:

- (i) Small size, (ii) high nuclear charge, (iii) a number of vacant orbitals of equivalent energy where the electrons donated by ligands are accommodated.
- 5. The neutral molecules, anions or cations which are directly linked with the central metal atom or ion in a complex ion are called **ligands**. The ligand at least consists one donor atom having a lone pair of electrons which it can donate to metal atom or ion. Ligands can be classified on the basis of number of donor atoms. They are termed monodentate, bidentate, tridentate, etc. The ligands having two or more donor groups are called polydentate. Polydentate ligand is known as **chelating ligand** if on coordination it results in the formation of a closed or cyclic ring structure. The complexes, thus, formed are called **chelates**.
- 6. The number of atoms of the ligands that are directly bound to the central metal atom or ion by coordinate bonds is known as coordination number of the metal atom or ion. It is actually the number of chemical bonds which the ligands form with central metal atom or ion. The most common coordination number are 4 or 6. The central metal atom or ion and the ligands that are directly attached to it are enclosed in a square bracket. This is called coordination sphere. It behaves as a single unit. The ions present outside the coordination sphere form ionisation sphere.

$$K_4Fe(CN)_6 \iff 4K^+ + [Fe(CN)_6]^{4-}$$
  
 $[Cu(NH_3)_4]SO_4 \iff [Cu(NH_3)_4]^{2+} + SO_4^{2-}$ 

Charge on the complex ion = oxidation number of metal ion + charge on the ligands



- 7. Effective atomic number (EAN) is defined as the resultant number of electrons with the metal atom or ion after gaining electrons from donor atoms after ligands.
  - EAN = atomic number of the metal number of electrons lost in ion formation + number of electrons gained from the donor atoms of the ligands.
- **8.** The following points are followed in naming complex compounds:
  - (i) Cation is named first followed by anion.
  - (ii) In the coordination sphere, the ligands are named alphabetically. Anionic ligands ending with -ide are named by replacing -ide by suffix -o or by replacing -e by -o. Ligands whose names end in -ite or -ate become -ito or -ato, i.e., by replacing the ending -e with -o. Neutral ligands are given the same names as the neutral molecules. However, H<sub>2</sub>O is named aqua and NH<sub>3</sub> ammine. Positively charged ligands have suffix -ium. If the number of a particular ligand is more than one, the number is indicated by using di, tri, tetra, penta, etc. However, when the name of the ligand includes a number, then bis, tris, etc., are used.

- (iii) The oxidation state of the central metal is shown by Roman numeral in bracket immediately following its name.
- (iv) Complex positive ions and neutral coordination compounds have no special ending but complex negative ions always end in the suffix -ate.
- Coordination compounds exhibit structural isomerism as well
  as stereoisomerism. Structural isomerism is displayed when
  different ligands are present within coordination spheres.
  The coordination compounds exhibit various types of
  structural isomerism.
  - (i) Ionisation isomerism: Isomers give different ions in solution.

Examples: [Co(NH<sub>3</sub>)<sub>5</sub>Br]Cl; [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Br.

- (ii) Hydrate isomerism: Isomers having  $H_2O$  as a ligand or as water of hydration.
  - **Examples:**  $[Cr(H_2O)_6]Cl_3;$   $[CrCl(H_2O)_5]Cl_2\cdot H_2O;$   $[CrCl_2(H_2O)_4]Cl\cdot 2H_2O.$
- (iii) Coordination isomerism: The ligands are interchanged in both the cationic and anionic ions.

  Examples: [Co(NH<sub>2</sub>)][Cr(NN<sub>2</sub>] [Cr(NH<sub>2</sub>)]

**Examples:**  $[Co(NH_3)_6][Cr(CN)_6];$   $[Cr(NH_3)_6]$   $[Co(CN)_6].$ 

- (iv) Linkage isomerism: This type of isomerism exists when ambidentate ligand is present.
- Examples: [Co(NH<sub>3</sub>)<sub>5</sub>ONO]Cl<sub>2</sub>; [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>] Cl<sub>2</sub>.

  10. Stereoisomerism: It arises on account of the different positions and arrangement of ligands in space around the metal ion. It is of two types: (a) geometrical and (b) optical. Geometrical isomerism is common in coordination number 4 (square planar) and coordination number 6 compounds. This type of isomerism is termed *cis-trans* isomerism. When the ligands occupy adjacent positions, the isomer is called *cis*form and when opposite positions, the isomer is termed *trans* isomer. The square planar complexes having general formulae *Ma*<sub>2</sub>*b*<sub>2</sub>, *Ma*<sub>2</sub>*bc* or *Mabcd* show *cis-trans* isomerism. Square planar complexes having unsymmetrical bidentate ligands can also show geometrical isomerism.

Geometrical isomerism is not observed in complexes of coordination numbers 2 and 3. Square planar complexes of the type  $Ma_4$ ,  $Ma_3b$  and  $Mab_3$  do not show geometrical isomerism. Geometrical isomerism is also not observed in tetrahedral complexes.

Octahedral complexes of the type  $Ma_4b_2$ ,  $Ma_2b_4$ ,  $Ma_4bc$  and  $Ma_3b_3$  exhibit geometrical isomerism.

11. A coordination compound which can rotate the plane of polarised light is said to be optically active. The optical isomers are pair of molecules which are non-superimposable mirror image of each other. The isomer which rotates the plane of polarised light to right direction is termed dextro while the isomer which rotates the plane of polarised light to left direction is termed laevo form. Optical isomerism is very common in octahedral complexes. Octahedral compounds of general formulae  $[Ma_2b_2c_2]^{n\pm}$ ,  $[M(AA)_3]^{n\pm}$ ,  $[M(AA)_2a_2]^{n\pm}$ ,  $[M(AA)_2ab]^{n\pm}$  and  $[M(AB)_3]^{n\pm}$  where AA = symmetrical bidentate ligands and AB = unsymmetrical bidentate ligands.

- 12. Werner, in 1893, proposed the coordination theory to explain the properties and structures of various metal ammines. The important postulates of the theory are:
  - (a) Every element exhibits two types of valency: (i) Primary valency and (ii) Secondary valency. Primary valency corresponds to oxidation state of metal and secondary valency represents the coordination number of the metal. Primary valency is satisfied by negative ions and is ionisable. The secondary valency is satisfied by neutral molecules or negative ions or both. This valency is nonionic. Metal and neutral molecules or negative ions which satisfy secondary valency are enclosed in square bracket and termed as coordination sphere.
  - (b) Every element tends to satisfy both its valencies. A negative ion when present in coordination sphere shows a dual behaviour. It satisfies both primary and secondary valencies. The presence of negative ion in the coordination sphere reduces the charge on the complex ion by the amount of charge possessed by it and the negative ions present in the coordination sphere are not ionised.
  - (c) The ligands in coordination sphere are directed towards fixed positions in space. The geometry of the complex ion depends on coordination number. If the coordination number is 6, the complex is octahedral. On the other hand, if the coordination number is 4, the geometry of the complex may be tetrahedral or square planar.
- 13. Valence bond theory describes the bonding in complexes in terms of two-electron, coordinate-covalent bonds resulting from overlap of filled ligand orbitals with vacant metal hybrid orbitals that point in the direction of the ligands: sp (linear);  $sp^3$  (tetrahedral);  $dsp^2$  (square planar) and  $d^2sp^3$

This theory explains with reasonable success the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to provide a quantitative interpretation of magnetic behaviour and explanation about optical properties of coordination compounds.

### **Examples:**

### (a) Octahedral complexes:

and  $sp^3d^2$  (octahedral).

(i) Inner orbital (low spin) complexes involving  $d^2sp^3$  hybridization:

 $[Fe(CN)_6]^{3-}$ ,  $[Co(CN)_6]^{3-}$ ,  $[Cr(NH_3)_6]^{3+}$ ,  $[Co(NH_3)_6]^{3+}$ , etc.

(ii) Outer orbital (high spin) complexes involving  $sp^3d^2$  hybridization:

 $[\text{CoF}_6]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{MnF}_6]^{3-}$ ,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ , etc.

- (b) Tetrahedral complexes involving  $sp^3$  hybridization:  $[NiCl_4]^{2-}$ ,  $[Cu(Cl_4)]^{2-}$ ,  $Ni(CO)_4$ ,  $[Zn(NH_3)_4]^{2+}$ , etc.
- (c) Square planar complexes involving  $dsp^2$  hybridization:  $[Ni(CN)_4]^{2-}$ ,  $[Cu(NH_3)_4]^{2+}$ , etc.
- 14. Crystal field theory assumes that the metal-ligand bonding is entirely ionic. Because of electrostatic repulsions between the d electrons and the ligands, the d-orbitals are raised in energy and are differentiated by an energy separation called

the crystal field splitting,  $\Delta$ . In octahedral complexes the  $d_z^2$ ,  $d_{x^2-y^2}$  orbitals (e.g., set of orbitals) have higher energy than  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals (e.g., set of orbitals). Tetrahedral complexes exhibit just opposite splitting pattern.

The colours of complexes are due to electronic transitions from one set of d-orbitals to another and the transition energies depend on the position of ligand in the spectrochemical series. Weak field ligands give small  $\Delta$  values and strong field ligands give large  $\Delta$  values. Crystal field theory accounts for magnetic properties of complexes in terms of the relative values of  $\Delta$  and the spin pairing energy. Small  $\Delta$  values favour high spin complexes (maximum number of unpaired d electrons) and large  $\Delta$  values favour low spin complexes.

15. In general, higher the charge density on the central ion, the greater is the stability of its complexes. Electronegativity of the central ion also influences the stability. The higher the oxidation state of the metal, the more stable is the complex. The more basic ligand forms the complex with greater stability. The cyano and ammine complexes are far more stable than those formed by halide ions.

Chalating ligands form more stable complexes as compared.

Chelating ligands form more stable complexes as compared to monodentate ligands.

- **16.** Coordination compounds are generally prepared by the application of :
  - (a) Ligand substitution reactions:  $[Cu(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> + 4NH<sub>3</sub> \longrightarrow [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> + 4H<sub>2</sub>O$
  - (b) Direct mixing of reagent:  $PtCl_2 + 2H_2N - CH_2 - CH_2 - NH_2 - Pt(en)_2Cl_2$
  - (c) Redox reaction:  $K_2Cr_2O_7 + 7H_2C_2O_4 + 2K_2C_2O_4 \longrightarrow 2K_3[Cr(C_2O_4)_3]$  $+6CO_2 + 7H_3C_2O_4 + 2K_2C_2O_4 \longrightarrow 2K_3[Cr(C_2O_4)_3]$
- 17. The complexes find applications in various fields:
  - (a) Analytical chemistry—Cu<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, etc., are tested in the form of complexes. Ca<sup>2+</sup>, Mg<sup>2+</sup> and Zn<sup>2+</sup> ions are estimated volumetrically by EDTA. Many ions are quantitatively estimated by using a number of organic ligands.
  - (b) Coordination complexes of transition metals exhibit a variety of colours. This forms the basis of colorimetric estimations.
  - (c) Complexes act as oxidation-reduction indicators and sequestering reagents. Hardness of water is estimated by use of EDTA.
  - (d) Silver and gold are extracted by the use of complex formation.
  - (e) Fixing of negative is done in photography by use of hypo solution. It forms soluble complex with silver bromide.
  - (f) During electroplating, complexes are used in electrolytic bath.
  - (g) Cis-platin, [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], is used in the treatment of cancer.

British anti-lewisite (BAL) is used as antidote for treating poisoning by As, Hg, Au, Bi, Pb and Cd.

(h) Haemoglobin is a complex of Fe, chlorophyll is a complex of Mg, vitamin B<sub>12</sub> is a complex of cobalt.

- 18. Compounds that contain at least one carbon-metal bond are called organometallic compounds. Organometallic compounds may be classified in three classes:
  - (a) Sigma ( $\sigma$ ) bonded complexes (b) pi ( $\pi$ ) bonded complexes (c) complexes containing both  $\sigma$  and  $\pi$ -bonding.

Grignard reagent (R—Mg—X), zinc compound: ( $R_2$ Zn), Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>, etc., are σ-bonded organometallic compounds. Zeise's salts, ferrocene, dibenzene chromium are  $\pi$ -bonded complexes. Metal carbonyls are examples of both  $\sigma$  and  $\pi$ -bonded organometallic compounds.

- 19. (a) Ligands with more than six donor groups form unstable rings due to steric hindrance.
  - (b) Chelating ligands form more stable complexes than the monodentate ligands. Chelates with five membered rings including metal atom are more stable if these do not contain double bonds. Chelates with six membered rings are more stable if the ligands contain conjugate double
  - (c) Complex formed with a cyclic polydentate ligand is more stable than complex formed with a non-cyclic ligand.
- **20.** (a) The complexes of the type  $MA_3B_3$  can form the following two types of geometrical isomers:

$$\begin{array}{c|c} NH_3 \\ H_3N & - & Cl \\ \hline \\ H_3N & - & Cl \\ \end{array}$$

Facial or fac-isomer

All the similar ligands occupy the same face of the octahedron.

$$H_3N_{\square}$$
  $C_1$   $C_1$   $C_2$   $C_3$   $C_4$   $C_4$   $C_5$   $C_6$   $C_1$ 

Meridional or mer-isomer

(b) In square planar complexes, positions, 1,2; 2,3; 3,4 and 1,4 are cis while 1,3 and 2,4 are trans with respect to each other. In octahedral complexes, positions 1,2; 1,3; 1,4 and 1,5 are cis while 1,6; 2,4 and 3,5 are trans with respect to each other.



Square planar



21. (a) Ferrocene  $[Fe(\eta^5 - C_5H_5)_2]$  and dibenzene chromium  $[Cr(\eta^6 - C_6H_6)_2]$  are called sandwiched compounds.

- (b) Potassium hexanitrocobaltate(III), K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] is called Fischer's salt.
- (c) Haemoglobin is a complex of Fe, chlorophyll is a complex of Mg and vitamin B<sub>12</sub> is a complex of Co.
- 22. (a) Organo-arsenic compounds are used as remedy for syphillis.
  - (b) Zeigler-Natta catalyst, R<sub>3</sub>Al, mixed with TiCl<sub>3</sub> or TiCl<sub>4</sub> is used in low temperature polymerisation of alkenes.
  - (c) Wilkinson's catalyst, (Ph<sub>3</sub>P)<sub>3</sub>RhCl is used in the hydrogenation of alkenes.
  - (d) Ethyl mercury chloride is used to prevent the infection of young plants.
  - Tetraethyl Lead (TEL) is an important anti-knock compound added to petrol used in interval combustion engines.
  - (f) Grignard reagent and several other organo metallics are good reagents for the synthesis of compounds.

# Subjective Type Questions

- 1. Indicate 'principal' and 'secondary' valencies of central metal ion in the following complexes:
  - (a)  $[Cr(NH_3)_6]Cl_3$
- (b)  $K_4[Fe(CN)_6]$
- (c)  $[Pt(NH_3)_2Cl_2]$
- (d)  $K_2[PtCl_4]$
- (e)  $[Co(NH_3)_5H_2O]Cl_3$
- (f) [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>
- Determine the effective atomic number of the metal atom in the following:
  - (a)  $[Cr(CO)_6]$
- (c) [Co(CN)<sub>6</sub>]<sup>4</sup>
- (b) [Fe(CN)<sub>6</sub>]<sup>3-</sup> (d) [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>

[Cr = 24; Fe = 26; Co = 27 and Ni = 28 as atomic numbers]

- 3. Write down the IUPAC names of the following complexes:
  - (i)  $K_4[Mo(CN)_8]$
- (ii)  $Co[(en)_2Cl(ONO)]^+$
- (iii) [Cr(P·Ph<sub>3</sub>)(CO)<sub>5</sub>]
- (iv)  $[Pt(NH_3)_4Cl_2][PtCl_4]$
- (v) (NH<sub>4</sub>)<sub>3</sub>[Cr(NCS)<sub>6</sub>]

- (vi)
- (vii) K[BF<sub>4</sub>]
- (viii) Cu<sub>2</sub>[Fe(CN)<sub>6</sub>]
- Write the formulae of the following complexes:
  - (a) Diamminechlorido (ethylenediamine) nitrito-N-platinum (IV) chloride.
  - (b) Calcium hexacyanoferrate (II).
  - Tetraamminecobalt (III)-µ-amino-µ-nitrotetraamminecobalt (III) nitrate.
  - (d) Dichlorido bis (ethylenediamine) cobalt (III) sulphate.
  - Sodium tetrahydroxoaluminate (III).
  - Potassium ethylenediamine tetraacetate ferrate (II).
  - (g) Hexaammine chromium(III) hexacyanocobaltate(III).
- Combination of Pt(IV), NH<sub>3</sub>, Cl<sup>-</sup> and K<sup>+</sup> results in the formation of seven complexes and one such complex is [Pt(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>4</sub>.

- (i) Write the formulae of the other six members of the
- (ii) Name these complexes according to the IUPAC system of nomenclature.
- (iii) Which will have highest molar conductivity?
- (iv) Which of these is non-ionic?
- (v) What is the coordination number and oxidation state of Pt in these complexes?
- How many ions per mole of the following complexes are present in their solutions?
  - (i)  $[Co(NH_3)(en)_2Cl]Cl_2$
- (ii)  $[Ag(NH_3)_2]Br$
- (iii) [Pt(NH<sub>3</sub>)<sub>4</sub>][PtCl<sub>4</sub>]
- (iv) [Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl<sub>2</sub>
- (v)  $Cu_2[Fe(CN)_6]$
- 7. Which of the following names are correct?
  - (i) K<sub>3</sub>[Fe(CN)<sub>5</sub>NO] : Potassium pentacyanonitrosyl ferrate (II).
  - (ii) Na<sub>2</sub> [Ni (EDTA)]: Sodium ethylenediamminetetraacetatonickel (I).
  - (iii) [Co(NH<sub>3</sub>)<sub>5</sub>CO<sub>3</sub>]Cl: Pentaamminecarbonatocobalt (III) chloride.
  - (iv)  $K_3[Al(C_2O_4)_3]$ : Potassium tris (oxalato) aluminate
  - (v)  $K_2[Zn(OH)_4]$
- : Potassium tetrahydroxozincate (II).
- (vi)  $K_2[PtF_6]$
- : Potassium hexafluoridoplatinate (IV).
- (vii) [Co(en)3]Cl3
- : Triethylenediamminecobalt (III)
- chloride.
- (viii) Hg[Co(CNS)<sub>4</sub>] : Mercury tetrathiocyanatocobalt (II).
- 8. What type of isomers are the following?
  - (i) [(CO)<sub>5</sub>MnSCN]
- and [(CO)<sub>5</sub>MnNCS]
- (ii)  $[Co(en)_3][Cr(CN)_6]$
- and [Cr(en)<sub>3</sub>] [Co(CN)<sub>6</sub>]
- (iii) [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>3</sub>]SO<sub>4</sub>
- and [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]NO<sub>3</sub>
- (iv)  $[Co(py)_2(H_2O)_2Cl_2]Cl$  and  $[Co(py)_2(H_2O)Cl_3]H_2O$
- Describe a simple chemical test that would allow you to distinguish between the compounds, [Co(NH<sub>3</sub>)<sub>5</sub>Br]SO<sub>4</sub> and [Co(NH3)5SO4]Br.
- 10. How many geometrical isomers are there for:
  - (a) [Co(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>], octahedral?
  - (b) [AuCl<sub>2</sub>Br<sub>2</sub>], square planar?
  - (c)  $[CoCl_2Br_2]^{2-}$ , tetrahedral?
- 11. What are the types of hybridization involved in the following geometrical shapes of the complex?
  - (a) Square planar
- (b) Tetrahedral
- (c) Octahedral
- 12. Explain the geometry and magnetic nature of the following complex ions on the basis of valence bond theory.
  - (i)  $[Cr(NH_3)_6]^{3+}$
- (iii)  $[FeF_6]^{3-}$

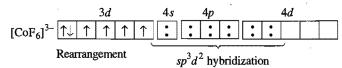
- (iv)  $[MnCl_4]^2$
- (ii) [Fe(CN)<sub>6</sub>]<sup>4-</sup> (v) [Ni(CN)<sub>4</sub>]<sup>2-</sup>
- (vi)  $[Cu(NH_3)_4]^{2+}$
- 13. Explain the following:
  - (i) All the octahedral complexes of Ni<sup>2+</sup> must be outerorbital complexes.

[Ans. 3d $Ni^{2+}$  configuration  $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow$ 

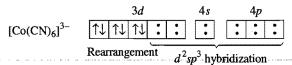
During rearrangement only one 3d-orbital may be made available by pairing the electrons. Thus, inner  $d^2sp^3$ 

hybridization is not possible. So, only  $sp^3d^2$  (outer) hybridization can occur.]

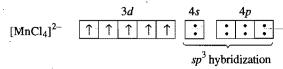
 $[CoF_6]^{3-}$  is paramagnetic but  $[Co(CN)_6]^{3-}$  is diamagnetic. [Ans. In  $[CoF_6]^{3-}$ ,  $Co^{3+}$  undergoes  $sp^3d^2$  hybridization. Four d-orbitals are singly occupied. Hence, it is paramagnetic.



In  $[Co(CN)_6]^{3-}$ ,  $Co^{3+}$  undergoes  $d^2sp^3$  hybridization. No-orbital is singly occupied. Hence, it is diamagnetic.]



(iii) The magnetic moment of [MnCl<sub>4</sub>]<sup>2</sup> is 5.92 B.M. [Ans. In [MnCl<sub>4</sub>]<sup>2-</sup> ion, Mn<sup>2+</sup> ion undergoes sp<sup>3</sup> hybridization. It contains 5d-orbitals singly occupied. Hence, it has high value of magnetic moment.]



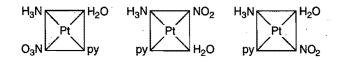
(iv) NH<sub>4</sub> ion does not form complexes.

[Ans. NH<sub>4</sub><sup>+</sup> ion does not act as ligand because nitrogen atom has no lone pair of electrons which it can donate to metal atom.]

(v) (SCN) shows linkage isomerism in coordination compounds.

[Ans. (SCN) group can coordinate with metal atom either through S-atom or N-atom giving two isomers. Thus, it shows linkage isomerism.]

(vi) Three geometrical isomers of the square planar complex,  $[Pt(NH_3)(H_2O)(py)(NO_2)]^+$ , are possible. [Ans.



Three different arrangements corresponding to three geometrical isomers are possible.]

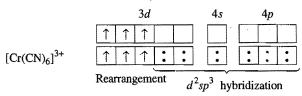
- 14. Find out the hybridization, geometry and magnetic moment of the complexes:
  - $[Co(MH_3)_6]^{34}$
- (ii) [Cr(CN)<sub>6</sub>]<sup>3</sup>-

[Ans. The oxidation state of cobalt in the complex is +3. The electronic configuration of Co<sup>3+</sup> ion is:

	34	d	4 <i>s</i>	4 <i>p</i>
	$\uparrow\downarrow$ $\uparrow$ $\uparrow$	1 1		
$[Co(NH_3)_6]^{3+}$	$\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow$			
	Rearrangen	nent d2	sn <sup>3</sup> hyb	ridization

Octahedral, zero magnetic moment.

The oxidation state of chromium in the complex is +3. The electronic configuration of Cr<sup>3+</sup> ion is:



Octahedral, mag. moment =  $\sqrt{3 \times (3+2)} = \sqrt{15} = 3.87$  B.M.]

- 15. Draw the structures of  $[Co(NH_3)_6]^{3+}$ ,  $[Ni(CN)_4]^{2-}$  and  $Ni(CO)_4$ . Write the hybridization of atomic orbitals of the transition metal in each case. [I.I.T. 2000]
- Deduce the structures of [NiCl<sub>4</sub>]<sup>2-</sup> and [Ni(CN)<sub>4</sub>]<sup>2-</sup> considering the hybridization. Calculate the magnetic moment (spin only) of the species. [I.I.T. 2002]
   [Ans. In [NiCl<sub>4</sub>]<sup>2-</sup>, CI is weak field ligand.

$$Ni_{28} \longrightarrow 3d^{8}4s^{2}4p^{0}$$

$$Ni^{2+} \text{ in } \longrightarrow \qquad \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \qquad \vdots \qquad \vdots \qquad \vdots$$

$$[NiCl_{4}]^{2-} \qquad \qquad sp^{3} \text{ hybridization}$$

:.  $[NiCl_4]^{2-}$  is a tetrahedral complex. Number of unpaired electrons in  $Ni^{2+} = 2$ 

Magnetic moment ' $\mu$ ' =  $\sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.82$  B.M. In [Ni(CN)<sub>4</sub>]<sup>2-</sup>, CN<sup>-</sup> is strong field ligand.

 $Ni^{4+}$  in  $\longrightarrow$   $T\downarrow T\downarrow T\downarrow T\downarrow$   $dsp^2$  hybridization

..  $[\text{Ni(CN)}_4]^{2-}$  is a square planar complex. Number of unpaired electrons in  $\text{Ni}^{2+} = 0$ Magnetic moment ' $\mu$ ' =  $\sqrt{n(n+2)} = 0$  ]

- 17. What are the main features of the ligand field theory?
- 18. How does crystal field theory explain?
  - (i) High spin and low spin states of complexes
  - (ii) Magnetism of complexes
  - (iii) Colour of the complexes.
- 19. (a) What are organometallic compounds? How are these compounds classified?
  - (b) How is ferrocene, Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> prepared? Draw its structure.
- **20.** (a) Describe at least three applications of coordination compounds.
  - (b) Describe the applications of organometallic compounds in homogeneous catalysis.
- 21. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

# Matching Type Questions

### Match the following:

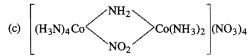
- 1. Double salt
- 2. Zeise's salt
- 3. Neutral molecule
- 4. EDTA
- 5. Ni(CO)<sub>4</sub>
- 6.  $[Cr(NH_3)_6]^{3+}$
- 7. Low spin complex
- 8. Glycine

- (a)  $[Co(NH_3)_3Cl_3]$
- (b) Hexadentate...
- (c) Bidentate
- (d) Paramagnetic
- (e)  $FeSO_4$ ·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O
- (f)  $K_4$ Fe(CN)<sub>6</sub>
- (g) Diamagnetic
- (h) An organometallic compound

# Answers

### Answers: Subjective Type Questions

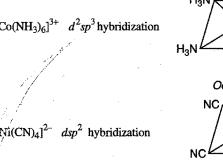
- 1. (a) 3 and 6 (b) 2 and 6 (c) 2 and 4 (d) 2 and 4 (e) 3 and 6 (f) 2 and 4.
- 2. (a) 36 (b) 35 (c) 37 (d) 38.
- 3. (i) Potassium octacyanomolybdate (IV) (ii) Chlorido bis (ethylene-diammine) nitrito-o-cobalt (III) ion (iii) Pentacarbonyl triphenylphosphinechromium (0) (iv) Tetraamminedichloridoplatinum (IV) Tetrachloridoplatinate (II) (v) Ammonium hexaisothiocyanato chromate (III) (vi) Tetraamminecobalt (III)-µ-amido-µ-peroxotetraammine cobalt (III) ion (vii) Potassium tetrafluoridoborate (III) (viii) Copper hexacyanoferrate (II).
- 4. (a)  $[Pt(NH_3)_2Cl(en)NO_2]Cl$
- (b)  $Ca_2[Fe(CN)_6]$

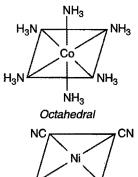


- (d)  $[Co(CN)_2Cl_2]Cl_3$
- (e)  $Na[Al(OH)_4]$
- (f)  $K_2[Fe(EDTA)]$
- (g) [Cr(NH<sub>3</sub>)<sub>6</sub>][Co(CN)<sub>6</sub>]
- 5. (i)  $[Pt(NH_3)_5Cl]Cl_3$ ;  $[Pt(NH_3)_4Cl_2]Cl_2$ ;  $[Pt(NH_3)_3Cl_3]$ ;  $[Pt(NH_3)_2Cl_4]$ ;  $[Pt(NH_3)Cl_5]^-$ ;  $[PtCl_6]^{2-}$ 
  - (ii) Pentaamminechloridoplatinum (IV) chloride; Tetraamminedichloridoplatinum (IV) chloride, Triammine trichlorido platinum (IV) chloride

- ride; Diamminetetrachloridoplatinum (IV); Amminepentachlorido platinate (IV) ion; Hexa chloridoplatinate (IV) ion.
- (iii) [Pt(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>4</sub> (iv) [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>] (v) 6 and 4.
- 6. (i) 3 mole of ions,  $[Co(NH_3)(en)_2Cl]^+ + 2Cl^-$  (ii) 2 mole of ions,  $[Ag(NH_3)_2]^+ + Br^-$  (iii) 2 mole of ions,  $[Pt(NH_3)_4]^{2+} + [PtCl_4]^{2-}$  (iv) 3 mole of ions,  $[Pt(NH_3)_4Cl_2]^{2+} + 2Cl^-$  (v) 3 mole of ions,  $2Cu^{2+} + [Fe(CN)_6]^{4-}$ .
- 7. (i), (iii), (v) and (vi) are correct.
- 8. (i) Linkage (ii) Coordination (iii) Ionisation (iv) Hydrate.
- [Co(NH<sub>3</sub>)<sub>5</sub>Br]SO<sub>4</sub> gives which precipitate with barium chloride solution while [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]Br gives light yellow precipitate with AgNO<sub>3</sub> solution.
- 10. (a) Two, cis- and trans-
- (b) Two, cis- and trans-
- (c) No isomerism is exhibited.
- 11. (a)  $dsp^2$  (b)  $sp^3$  (c)  $d^2sp^3$  or  $sp^3d^2$ .
- 12. (i) Octahedral, Paramagnetic (ii) Octahedral, Diamagnetic
  - (iii) Octahedral, Paramagnetic (iv) Tetrahedral, Paramagnetic
  - (v) Square planar, Diamagnetic (vi) Square planar, Paramagnetic.

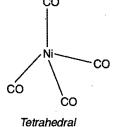
 $[Co(NH_3)_6]^{3+}$   $d^2sp^3$  hybridization





Square planar

[Ni(CO)<sub>4</sub>] sp<sup>3</sup> hybridization



Answers: Matching Type Questions

# ILLUSTRATIONS OF OBJECTIVE QUESTIONS

- 1. Highest molar conductivity is exhibited by:
  - (a) [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub>
- (b) [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl
- (c) [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>
- (d) [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]

Ans. (a)

[Hint: [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> gives maximum number of ions in solution. Thus, it shows highest molar conductivity.  $[Co(NH_3)_6]Cl_3 \Longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^{-}$ Total ions = 41

- The complex,  $[Co(NH_3)_4Cl_2]^+$  is known to exist in two different coloured forms. This is due to:
  - (a) ionisation isomerism
- (b) optical isomerism
- (c) geometrical isomerism
- (d) linkage isomerism

Ans. (c)

- 3. The IUPAC name of  $[Pt(NH_3)_4Cl_2][PtCl_4]$  is:
  - (a) tetraamminedichloridoplatinum (IV) tetrachloridoplatinate (III)
  - (b) tetraamminedichloridoplatinum (II) tetrachloridoplatinate (III)
  - (c) tetraamminedichloridoplatinum (III) tetrachloridoplatinate (II)
  - (d) tetraamminedichloridoplatinum (IV) tetrachloridoplatinate (II) Ans. (d)
- Which one of the following cyano complexes would exhibit the lowest value of paramagnetic behaviour?

[A.LE.E.E. 2005]

- (a)  $[Cr(CN)_6]^{3-}$
- (b) [Co(CN)<sub>6</sub>]
- (c)  $[Fe(CN)_6]^3$
- (d) [Mn(CN)<sub>6</sub>]

Ans. (b)

[Hint :  $Co^{3+}$ , E.C. = [Ar]  $3d^6$ 

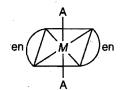
No unpaired electron paramagnetism = 0

- 5. In which of the following pairs both the complexes show optical isomerism? [A.I.I.M.S. 2005]
  - (a) cis-[Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>3-</sup>, cis-[Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]
  - (b) [Co(en)<sub>3</sub>]Cl<sub>3</sub>, cis-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl

- (c) [PtCl (dien)]Cl, [NiCl<sub>2</sub>Br<sub>2</sub>]<sup>2-</sup>
- (d)  $[Co(NO_3)_3(NH_3)_3]$ , cis- $[Pt(en)_2Cl_2]$

Ans. (b)

Two complexes given below are:





- (a) geometrical isomers
- (b) position isomers
- (c) optical isomers
- (d) identical

Ans. (d)

[Hint: Both represent the same molecule.]

- 7. The number of geometrical isomers of  $[Co(NH_3)_3(NO_2)_3]$  are:
  - (a) 2

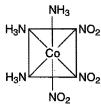
(b) 3

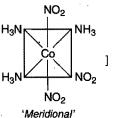
(c) 4

(d) nil

Ans. (a)

[Hint: The complex exhibits two geometrical isomers (i) facial and (ii) meridional.





- 'Facial' Which of the following is a  $\pi$ -acid ligand?
  - (a) NH<sub>3</sub>

(c) F

(d) H<sub>2</sub>N—CH<sub>2</sub>—CH<sub>2</sub>—NH<sub>2</sub>

Ans. (b)

[Hint: Ligands which are capable of accepting an appreciable amount of  $\pi$  electron density from the metal atom into  $\pi$ or  $\pi^*$  orbitals of their own are called  $\pi$ -acceptor or  $\pi$ -acid ligands such as CO.]

- **9.** Wilkinson's catalyst is:
  - (a) TiCl<sub>4</sub> and Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>
- (b)  $[(Ph_3P)_3RhCl]$
- (c) TiCl<sub>4</sub> and (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P Ans. (a)
- (d) none of these
- 10. Which of the following systems has maximum number of unpaired electrons or maximum paramagnetism?
  - (a)  $d_{-}^{4}$  (octahedral)
- (c)  $d^7$  (octahedral)
- (b)  $d^9$  (octahedral) (d)  $d^5$  (octahedral)

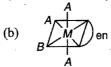
Ans. (d)

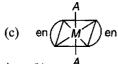
[Hint:  $d^5$  system has five unpaired electrons.]

- 11. The tetrahedral crystal field splitting is only . . . . of the octahedral splitting.
  - (a) 1/9
- (b) 2/9
- (c) 4/9
- (d) 5/9

- Ans. (c)
- 12. Which order is correct in spectrochemical series of ligands?
  - (a)  $Cl^{-} < F^{-} < [C_2O_4]^{2^{-}} < NO_2^{-} < CN^{-}$
  - (b)  $CN < [C_2O_4]^2 < Cl < NO_2 < F$
  - (c)  $[C_2O_4]^2 < F^- < Cl^- < NO_2^- < CN^-$
  - (d)  $F^- < Cl^- < NO_2^- < CN^- < [C_2O_4]^{2-}$
- 13. The phenomenon of optical activity will be shown by:









- Ans. (b)
- 14. The number of isomers possible for square planar complex, K<sub>2</sub>[PdClBr<sub>2</sub>SCN] are:
  - (a) 2

(b) 3

(c) 4

(d) 6

Ans. (c)

[Hint: Two geometrical isomers and two linkage isomers (-SCN

- 15. The pair in which both species have same magnetic moment (spin only value) is: [A.I.I.M.S. 2006]
  - (a)  $[Cr(H_2O)_6]^{2+}$ ,  $[CoCl_4]^{2-}$
  - (b)  $[Cr(H_2O)_6]^{2+}$ ,  $[Fe(H_2O)_6]^{2+}$
  - (c)  $[Mn(H_2O)_6]^{2+}$ ,  $[Cr(H_2O)_6]^{2+}$
  - (d)  $[CoCl_4]^{2-}$ ,  $[Fe(H_2O)_6]^{2+}$

Ans. (b)

[Hint: Same magnetic moment = Same number of unpaired electrons

$$=\sqrt{n(n+2)}$$

where n = number of unpaired electrons

 $Co^{2+} = 3d^7$ , 3 unpaired electrons

 $Cr^{2+} = 3d^4$ , 4 unpaired electrons  $Mn^{2+} = 3d^5$ , 5 unpaired electrons

 $Fe^{2+} = 3d^6$ , 4 unpaired electrons]

- 16. The pair in which both species have iron is: [A.I.I.M.S. 2006]
  - (a) nitrogenase, cytochromes
  - (b) carboxypeptidase, haemoglobin
  - (c) haemoglobin, nitrogenase
  - (d) haemoglobin, cytochromes Ans. (d)
- 17. The ligands in anticancer drug 'cis-platin' are:

[A.I.I.M.S. 2006]

- (a) NH<sub>3</sub>, Cl
- (b) NH<sub>3</sub>, H<sub>2</sub>O
- (c) Cl, H<sub>2</sub>O
- (d) NO, Cl

Ans. (a)

18. Match List-I with List-II and select the correct answer using codes given ahead in the lists:

LIST-1	List-II
Metal ions	Magnetic moments (B.M.)
A. Cr <sup>3+</sup>	1. √35
B. Fe <sup>2+</sup>	2. $\sqrt{30}$
C. Ni <sup>2+</sup>	3. $\sqrt{24}$
D. Mn <sup>2+</sup>	4. $\sqrt{15}$
	5 /6

- (a) A-1, B-3, C-5, D-4
- (b) A-2, B-3, C-5, D-1
- (c) A-4, B-3, C-5, D-1
- (d) A-4, B-5, C-3, D-1

[Hint: Magnetic moment =  $\sqrt{n(n+2)}$ 

$$Cr^{3+}$$
— $3d^3 = \sqrt{3 \times 5} = \sqrt{15}$   
 $Fe^{2+}$ — $3d^6 = \sqrt{4 \times 6} = \sqrt{24}$   
 $Ni^{2+}$ — $3d^8 = \sqrt{2 \times 4} = \sqrt{8}$   
 $Mn^{2+}$ — $3d^5 = \sqrt{5 \times 7} = \sqrt{35}$ 

- 19. In Fe(CO)<sub>5</sub>, the Fe-C bond possesses: [A.LE.E.E. 2006]
  - (a)  $\pi$  character only
- (b) σ character only
- (c) ionic character only
- (d) both  $\pi$  and  $\sigma$  characters

Ans. (d)

- **20.**  $[Cr(H_2O)_6]Cl_3$  (at. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of 3d electrons in the chromium present in the complex is: [C.B.S.E. 2006]
  - (a)  $3d_{xy}^1$ ,  $3d_{yz}^1$ ,  $3d_{zx}^1$
  - (b)  $3d_{xy}^1$ ,  $3d_{yz}^1$ ,  $3d_{zz}^1$
  - (c)  $3d_{(x^2-v^2)}^1$ ,  $3d_{z^2}^1$ ,  $3d_{xz}^1$
  - (d)  $3d_{xy}^1$ ,  $3d_{(x^2-y^2)}^1$ ,  $3d_{yz}^1$

[Hint: Magnetic moment indicates that there are three unpaired electrons present in chromium. These must be present in lower energy orbitals which are  $3d_{xy}$ ,  $3d_{yz}$  and  $3d_{xz}$ .]

# **OBJECTIVE QUESTIONS**



**Note:** Choose the correct answer out of given alternatives for each question.

l.	Ethylenediamine is an example of a ligand.		(b) tetracarbonyl nickelate(II)	
	(a) monodentate $\Box$ (b) bidentate $\Box$		(c) tetracarbonyl nickel(0)	
	(c) tridentate $\Box$ (d) hexadentate $\Box$		(d) tetracarbonyl nickel(II)	
2.	How many EDTA molecules are required to make an	14.	The number of chloride ions which would be precipit	tated,
	octahedral complex with a Ca <sup>2+</sup> ion? [A.I.E.E.E. 2006]		when CrCl <sub>3</sub> ·4NH <sub>3</sub> is treated with silver nitrate solution	:
•	(a) Six $\Box$ (b) Three $\Box$		(a) 3	
	(c) One $\Box$ (d) Two $\Box$		(c) 1	
	[Hint: Only one molecule is required as EDTA is a hexadentate	15.	[Co(NH <sub>3</sub> ) <sub>5</sub> Br]SO <sub>4</sub> and [Co(NH <sub>3</sub> ) <sub>5</sub> SO <sub>4</sub> ]Br are related to	each
	ligand.]		other as:	
3.	The coordination number and oxidation number of $X$ in the		(a) ionisation isomers	
	given compound $[X(NH_3)_5(SO_4)]Cl$ will be:		(c) coordination isomers   (d) geometrical isomers	
	[Haryana (P.M.T.) 2006]	16.	[Co(NH <sub>3</sub> ) <sub>5</sub> NO <sub>2</sub> ]Cl <sub>2</sub> and [Co(NH <sub>3</sub> ) <sub>5</sub> ONO]Cl <sub>2</sub> are related to	each
	(a) 10 and 3		other as:	
	(c) 6 and 3		(a) geometrical isomers	
4.	Which one will give Fe <sup>3+</sup> ions in solution?		(c) coordination isomers $\Box$ (d) ionisation isomers	
	(a) $[Fe(CN)_6]^{3-}$	17.	Which of the following shows structural, geometrical	l and
	(b) $[Fe(CN)_6]^{2-}$		optical isomerism?	*
	(c) $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$		(a) $[Co(en)(NH_3)_2Cl_2]Cl$	
	(d) $Fe_2(SO_4)_3$		(b) [Co(PPh <sub>3</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]Cl	
5.	Which of the following is non-ionisable?		(c) $[Co(en)_3]Cl_3$	-📮
	(a) $Pt(NH_3)_2Cl_4$ $\Box$ (b) $Pt(NH_3)_3Cl_4$ $\Box$		(d) $[Co(en)_2Cl_2]Br$	
	(c) $Pt(NH_3)_4Cl_4$ $\Box$ (d) $Pt(NH_3)_6Cl_4$ $\Box$	18.	Which one of the following does not give a white preci	pitate
6.	What is the coordination number of Cr in $K_3Cr(ox)_3$ ?		with silver nitrate solution?	
	(a) 6		(a) $[Co(NH_3)_6]Cl_3$	
	(c) 4		(c) $[Co(NH_3)_4Cl_2]Cl_2$ $\square$ (d) $[Co(NH_3)_3Cl_3]$	. $\square$
7.	What is the oxidation state of iron in $K_4$ Fe(CN) <sub>6</sub> ?	19.	Which of the following has the highest molar conduc	tivity
	(a) 6		in solution?	
	(c) 3 $\square$ (d) 2 $\square$		(a) $[Pt(NH_3)_6]Cl_4$ $\Box$ (b) $[Pt(NH_3)_5Cl]Cl_3$	
8.	What is the value of $x$ in the $[Ni(CN)_4]^x$ complex ion?		(c) $[Pt(NH_3)_4Cl_2]Cl_2$	
	(a) +2	20.	Geometrical isomerism is found in coordination compo	ounds
	(c) 0		having coordination number:	
9.	A complex compound in which the oxidation number of metal		(a) 2	
	is zero: [C.E.T. (Karnataka) 2008]		(c) 4 (tetrahedral) $\Box$ (d) 6	
	(a) $[Ni(CO)_4]$ $\Box$ (b) $[Pt(NH_3)_4]Cl_2$ $\Box$ (c) $K_4[Fe(CN)_6]$ $\Box$ (d) $K_3[Fe(CN)_6]$ $\Box$	21.	Which one of the following will be able to show geome	
10.	12 1 702		isomerism? [B.V.(Pune)	
10.	The EAN of cobalt in the complex ion $[Co(en)_2Cl_2]^+$ is: (a) 27 $\Box$ (b) 36 $\Box$		(a) $MA_4$	닏
	(a) 27	200	(c) $MABCD$	
11.		22.	Optical isomerism is not shown by the complex:	
11.	sulphate is:	ŀ	(a) $[Cr(ox)_3]^{3-}$	닏
	(a) $[Co(en)_2SO_4]$ $\Box$ (b) $[Co(en)_3SO_4]$ $\Box$	'	(b) $[Co(en)_2Cl_2]^+$ (cis-form).	. 🔲
	(c) $[Co(en)_3]_2SO_4$ $\Box$ (d) $[Co(en)_3]_2(SO_4)_3$ $\Box$		(c) $[Co(en)_2Cl_2]^+$ (trans-form)	
12.	The IUPAC name for the complex $[Co(NH_3)_5(NO_2)]Cl_2$ is:		(d) $[Cr(en)_3]^{3+}$	
	[A.I.E.E.E. 2006]		ox=oxalate; en=ethylenediamine	
	(a) nitrito- <i>n</i> -pentaammine cobalt (III) chloride	23.	Theoretically, the number of geometrical isomers expect	ed for
	(b) nitrito- <i>n</i> -pentaammine cobalt (II) chloride		octahedral complex, [Mabcdef] is:	_
	(c) pentaammine nitrito- <i>n</i> -cobalt (II) chloride		(a) 0	
	(d) pentaammine nitrito-n-cobalt (III) chloride	,	(c) 12	
13.		24.	The IUPAC name of complex, $K_3[Al(C_2O_4)_3]$ is:	
	(a) tetracarbonyl nickelate(0)		(a) potassium alumino oxalate	
	•		(b) potassium trioxalatoaluminate(III)	

	'				
	(c) potassium aluminium(III) oxalate		37.	Which one of following high spin complexes has the largest	
	(d) potassium trioxalatoaluminate(VI)			C.F.S.E. (crystal field stabilisation energy):	
25.	The complex that violates the EAN is:			(a) $[Cr(H_2O)]^{3+}$	
	(a) potassium ferrocyanide			(c) $[Mn(H_2O)_6]^{2+}$	
	(b) potassium ferricyanide			[Hint: Cation with higher oxidation state has a larger value of	
	(c) tetracarbonyl nickel			C.F.S.E. and C.F.S.E. decreases with increase of the	
	(d) hexaammine cobalt(III) chloride		20	number of electrons.]	
26.	The hybridization in Ni(CO) <sub>4</sub> is:	_	ĺ	The complex having the molecular composition,	
	(a) $sp_3$ $\square$ (b) $sp_3^2$			$[\text{Co(NO}_2)_2(\text{SCN})(\text{en})_2]$ Br exhibits:	
	(c) $sp^3$			(a) linkage isomerism	
27.	$K_4[Fe(CN)_6]$ is called:		1	(c) cis-trans isomerism  (d) all of these	
	(a) potassium hexacyanoferrate(II)		ł	Which one is not an organometallic compound?	
	(b) potassium ferricyanate		1	(a) $RMgX$ $\Box$ (b) $(C_2H_5)_4Pb$ $\Box$	
	(c) potassium ferricyanide			(c) $(CH_3)_4Sn$ $\square$ (d) $C_2H_5ONa$ $\square$	
	(d) prussian blue		40.	The formula of the ferrocene is:	
28.	The hybridization of Fe in $K_3[Fe(CN)_6]$ is:			(a) $[(C_5H_5)_2Fe]$ $\Box$ (b) $[Fe(CN)_6]^{3-}$ $\Box$	
,	(a) $sp^3$ $\Box$ (b) $dsp^3$		l .	(c) $[Fe(CN)_6]^2$ $\Box$ (d) $[Fe(CO)_5]$ $\Box$	
	(c) $sp^3d^2$		41.	$\pi$ -bonding is not involved in:	
29.	The complex, [Ni(CN) <sub>4</sub> ] <sup>2-</sup> has:	_	1	(a) ferrocene □ (b) dibenzene chromium □ (c) Zeise's salt □ (d) Grignard reagent □	
	(a) linear structure $\Box$ (b) tetrahedral structure		42.	(c) Zeise's salt	
	(c) square planar structure		42.	(a) rhodium	
20	(d) octahedral structure			(c) aluminium	
30.	All ligands are:		43.	Arrange the following in order of decreasing number of	
	(a) Lewis acids		15.	unpaired electrons:	
31	Which of the following is paramagnetic?	<u></u>		(i) $[Fe(H_2O)_6]^{2+}$ (ii) $[Fe(CN)_6]^{3-}$	
51.	(a) Potassium ferrocyanide			(i) $[Fe(H_2O)_6]^{2+}$ (ii) $[Fe(CN)_6]^{3-}$ (iv) $[Fe(H_2O)_6]^{3+}$	
	(b) Potassium ferricyanide			(a) (i), (ii), (iii), (iv) $\square$ (b) (iv), (ii), (i), (iii) $\square$	
	(c) Hexaammine cobalt(III) chloride			(c) (ii), (iii), (i), (iv) $\square$ (d) (iv), (i), (ii), (iii) $\square$	
	(d) Tetracarbonyl nickel(0)			[Hint: (iv), (i), (ii) and (iii) have 5, 4, 1 and 0 number of unpaired	
32.	Among the following ions which one has the highest p	ara-	l	electrons respectively.]	
	magnetism?		44.	Which of the following systems has maximum number of	•
	(a) $[Cr(H_2O)_6]^{3+}$			unpaired electrons?	
	(c) $[Cu(H_2O)_6]^{2+}$		ļ	(a) $d^4$ (octahedral, low spin)	<u>-</u>
	[Hint: Larger the number of unpaired electrons, the more i	t has	der Alle Control	(b) $d^6$ (tetrahedral) $\Box$ (c) $d^6$ (octahedral, low spin) $\Box$	
	paramagnetism. The outer configurations are; $Cr^{3+}$ - $Fe^{2+}$ - $3d^6$ ; $Cu^{2+}$ - $3d^9$ ; $Zn$ - $3d^{10}$ ]	$-3d^{3}$ ;		(c) $d^6$ (octahedral, low spin) $\Box$ (d) $d^9$ (octahedral) $\Box$	
			45.	The IUPAC name of $K_3[Fe(CN)_6]$ is: [A.I.E.E.E. 2005]	
33.	Which one of the following is paramagnetic in nature?		43.	(a) potassium ferrocyanide	
	(a) $Ni(CO)_4$			(b) potassium ferricyanide	
	(c) $[NiCl_4]^{2-}$			(c) potassium hexacyanoferrate(II)	ĺ
34.	Which one of the following complexes is diamagnet	ic in		(d) potassium hexacyanoferrate(III)	1
	nature?		46.	The oxidation number of Pt in $[Pt(C_2H_4)Cl_3]^-$ is:	
	(a) $[Cr(NH_3)_6]^{3+}$			(a) $+1$ $\square$ (b) $+2$ $\square$	
	(c) $[Co(NH_3)_6]$ $\Box$ (d) $[Fe(H_2O)_6]^{2+}$			(c) $+3$ $\square$ (d) $+4$ $\square$	j
35.	Which of the following complexes does not have tetrahe	edral	47.	Amongst Ni(CO) <sub>4</sub> , [Ni(CN) <sub>4</sub> ] <sup>2-</sup> and [NiCl <sub>4</sub> ] <sup>2-</sup> :	
•	geometry?			(a) $Ni(CO)_4$ and $[NiCl_4]^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$	-
	(a) Ni(CO) <sub>4</sub> (diamagnetic)			is paramagnetic	]
	(b) [MnCl <sub>4</sub> ] <sup>2-</sup> (5 unpaired electrons)			(b) [NiCl <sub>4</sub> ] <sup>2</sup> and [Ni(CN) <sub>4</sub> ] <sup>2</sup> are diamagnetic and [Ni(CO) <sub>4</sub> ]	1
	(c) [Ni(CN) <sub>4</sub> ] <sup>2-</sup> (diamagnetic)		-	is paramagnetic	]
	(d) [NiCl <sub>4</sub> ] <sup>2-</sup> (2 unpaired electrons)			(c) Ni(CO) <sub>4</sub> and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[NiCl_4]^{2-}$ is	3
36.	The complex $[Pt(NH_3)_4]^{2+}$ has structure.			paramagnetic $\square$	]
20,	(a) square planar			(d) Ni(CO) <sub>4</sub> is diamagnetic and $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are	3
	(c) pyramidal			paramagnetic	_

48.	Identify the complexes which are expected to be coloured:		(a) complex salt $\Box$ (b) double salt $\Box$
	(a) $[Ti(NO_3)_4]$		(c) normal salt $\Box$ (d) none of these $\Box$
	(c) $[Cr(NH_3)_6]^{3+}3Cl^-$	60.	Which of the following gives maximum number of isomers?
	[Hint: $\text{Ti}^{4+} = 3d^0$ ; $\text{Cu}^+ = 3d^{10}$ ; $\text{Cr}^{3+} = 3d^3$ ; $\text{V}^{3+} = 3d^2$ ]		[C.B.S.E. 2001]
49.	Vitamin B-12 contains:		(a) $[Co(NH_3)_4Cl_2]$ $\Box$ (b) $[Ni(en)(NH_3)_4]^{2+}$ $\Box$
	(a) cobalt		(c) $[Ni(C_2O_4)(en)_2]$ $\square$ (d) $[Cr(SCN)_2(NH_3)_4]^+$ $\square$
	(c) iron $\Box$ (d) nickel $\Box$	61.	Coordination number of Ni in $[Ni(C_2O_4)_3]^{4-}$ is:
50.	Find out the wrong statement for an octahedral complex:		[C.B.S.E. 2001]
	(a) An ion with $d^5$ configuration has one unpaired electron		(a) 3
	both in weak and strong fields.		(c) 4
	(b) A central metal ion with $d^8$ configuration has two	62.	Which of the following organometallic compounds is $\sigma$ and
	unpaired electrons.		$\pi$ bonded? [C.B.S.E. 2001]
	(c) An ion with $d^6$ configuration is diamagnetic in a strong		(a) $[\text{Fen}^5(\text{C}_5\text{H}_5)_2]$
	field.		(c) $[Co(CO)_5NH_3]^{2+}$ $\square$ (d) $[Al(CH_3)_3]$ $\square$
	(d) In $d^4$ , $d^5$ , $d^6$ and $d^7$ configurations, weak and strong field	63.	Which statement is incorrect? [C.B.S.E. 2001]
	complexes have different number of unpaired electrons.□		(a) Ni(CO) <sub>4</sub> —Tetrahedral, paramagnetic
	[Hint: A $d^5$ ion has 5 unpaired electrons in weak field.]		(b) $[Ni(CN)_4]^2$ —Square planar, diamagnetic
51.			* * * * * * * * * * * * * * * * * * *
	(a) $Na_2[CuCl_4]$ $\square$ (b) $Na_2[CdCl_4]$ $\square$		(c) [Ni(CO) <sub>4</sub> ]—Tetrahedral, diamagnetic
			(d) $[NiCl_4]^{2-}$ —Tetrahedral, paramagnetic
		64.	Which of the following cannot show linkage isomerism?
52.	The number of geometrical isomers of [Co(NH <sub>3</sub> ) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ] is:		[D.C.E. 2001]
	$\begin{array}{cccc} \text{(a) } 0 & & \Box & \text{(b) } 2 & & \Box \\ \text{(c) } 2 & & \Box & \text{(d) } 4 & & \Box \end{array}$		(a) $NO_2^-$
52	(c) 3		(c) $CN^-$
53.	The total number of possible isomers of the compound,	65.	Consider the following complex;
	$[Cu(NH_3)_4][PtCl_4]$ , are:		[Co(NH <sub>3</sub> ) <sub>5</sub> CO <sub>3</sub> ]ClO <sub>4</sub>
	(a) 3		the coordination number, oxidation number, number of $d$
	(c) 4		electrons and number of unpaired $d$ electrons on the metal
54.	The geometry of Ni(CO) <sub>4</sub> and Ni(PPH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> are:		are respectively: [S.C.R.A. 2001]
	(a) both square planar		(a) $6, 3, 6, 0$
	(b) tetrahedral and square planar respectively □	1	(c) $7, 1, 6, 4$
	(c) both tetrahedral	66.	In electroplating of copper, K [Ag(CN) <sub>2</sub> ] is used instead of
	(d) square planar and tetrahedral respectively		AgNO <sub>3</sub> . The reason is: [C.B.S.E. 2002]
55.	What is the shape of Fe(CO) <sub>5</sub> molecule? [C.B.S.E. 2000]		(a) a thin layer of Ag is formed on Cu
	(a) Tetrahedral		(b) more voltage is required
	(c) Trigonal bipyramidal □ (d) Square pyramidal □		(c) $Ag^+$ ions are completely removed from solution $\Box$
56.			(d) less availability of Ag <sup>+</sup> ions, as Cu cannot displace Ag
	occurring extensively in living world? [C.B.S.E. 2000]		from $[Ag(CN)_2]^-$ ion
	(a) Haemoglobin	67.	
	(c) Florigen		[C.E.T. (Chandigarh) 2002]
57.	The complex ion which has no $d$ electrons in the central metal		(a) $[Co(en)_2Cl_2]^+$
	atom is (At. No. $Cr = 24$ , $Mn = 25$ , $Fe = 26$ , $Co = 27$ ):		(c) $[Co(NH_3)_4Cl_2]^+$
	[I.I.T. (S) 2001]	68.	In $[Cr(C_2O_4)_3]^{3-}$ , the isomerism shown is:
	(a) $[MnO_4]^-$		[A.I.E.E.E. 2002]
	(c) $[Fe(CN)_6]^{3-}$ $\Box$ (d) $[Cr(H_2O)_6]^{3+}$ $\Box$		(a) ligand $\Box$ (b) optical $\Box$
58.	The correct order of hybridization of the central atom in	1	(c) geometrical $\Box$ (d) ionisation $\Box$
	following species NH <sub>3</sub> , [PtCl <sub>4</sub> ] <sup>2-</sup> , PCl <sub>5</sub> , BCl <sub>3</sub> is (At. No. of	69.	Atomic numbers of Cr and Fe are respectively 25 and 26,
	Pt = 78): [L1.T. (S) 2001]	.	which of the following is paramagnetic with spin of electron?
	(a) $dsp^2$ , $dsp^3$ , $sp^2$ and $sp^3 \square$ (b) $sp^3$ , $dsp^2$ , $dsp^3$ , $sp^2 \square$		[C.B.S.E. 2002]
			(a) $Cr(CO)_6$
ξO	(c) $dsp^2$ , $sp^2$ , $dsp^3$ , $sp^3$ $\Box$ (d) $dsp^2$ , $sp^3$ , $sp^2$ , $dsp^3$ $\Box$		(c) $[Fe(CN)_6]^{4-}$
59.	e e	70.	The hypothetical complex chlorodiaquatriammine cobalt (III)
	give test for one of them in solution. Such salts are:		chloride can be represented as : [C.B.S.E. 2002]

		_	•
	(a) $[CoCl(NH_3)_3(H_2O)_2]Cl_2$	81.	The complex used as an anticancer agent is:
	(b) $[Co(NH_3)_3H_2OCl_3]$		[A.I.I.M.S. 2003; B.H.U. 2007]
	(c) $[Co(NH_3)_3(H_2O)Cl]$ $\Box$ (d) $[Co(NH_3)_3(H_2O)_3Cl_3]$ $\Box$		(a) $mer$ -[Co(NH <sub>3</sub> ) <sub>3</sub> Cl <sub>3</sub> ] $\square$ (b) $cis$ -[PtCl <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] $\square$
71.	The type of isomerism present in nitropentaammine		(c) $cis$ - $K_2[PtCl_2Br_2]$ $\square$ (d) $Na_2[CoCl_4]$ $\square$
	chromium (III) chloride is: [A.I.E.E.E. 2002]	82.	The ligand called $\pi$ -acid is: [A.I.I.M.S. 2003]
	(a) optical		(a) CO $\Box$ (b) NH <sub>3</sub> . $\Box$
	(c) ionisation		(c) $C_2O_4^{2-}$ $\square$ (d) ethylene diamine $\square$
77	Development of a photographic plate involves the use of:	83.	The effective atomic number of cobalt in the complex
72.		05.	$[\text{Co(NH}_3)_6]^{3+}$ is: [P.E.T. (M.P.) 2003]
	[P.M.T. (Kerala) 2003]		(a) 36 $\square$ (b) 33 $\square$
	(a) an oxidising agent $\Box$ (b) a complexing agent $\Box$	]	(a) 30
	(c) a neutralising agent $\Box$ (d) a precipitating agent $\Box$	04	
70	(e) a reducing agent □	84.	The possible number of optical isomers in $[Co(en)_2Cl_2]^{+}$ are:
73.	In the coordination compound $K_4[Ni(CN)_4]$ , the oxidation		[P.E.T. (M.P.) 2003]
	state of nickel is: [A.I.E.E.E. 2003]		(a) 2
	(a) $-1$		(c) 4
	(c) +1	85.	Mixture of $(X) = 0.02$ mole of $[Co(NH_3)_5SO_4]Br$ and $0.02$ mole
74.	One mole of the complex compound Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sub>3</sub> , gives 3		of [Co(NH <sub>3</sub> ) <sub>5</sub> Br] SO <sub>4</sub> was prepared in 2 litre of solution;
	moles of ions on dissolution in water. One mole of the same		litre of mixture $[X]$ + excess AgNO <sub>3</sub> $\longrightarrow$ $[Y]$
	complex reacts with two moles of AgNO <sub>3</sub> solution to yield		l litre of mixture $[X]$ + excess $BaCl_2 \longrightarrow [Z]$
	two moles of $AgCl(s)$ . The structure of the complex is:		No. of moles of $[Y]$ and $[Z]$ are: [I.I.T. (S) 2003]
	[A.I.E.E.E. 2003]		(a) 0.01,0.01
	(a) $[Co(NH_3)_5Cl]Cl_2$		(c) $0.01,0.02$ $\Box$ (d) $0.02,0.02$ $\Box$
	(b) [Co(NH <sub>3</sub> ) <sub>3</sub> Cl <sub>3</sub> ]·2NH <sub>3</sub>	86.	In the process of extraction of gold,
	(c) $[Co(NH_3)_4Cl_2]Cl\cdot NH_3$	1	Roasted gold ore + $CN^- + H_2O \longrightarrow [X] + OH^-$
	(d) $[Co(NH_3)_4Cl]Cl_2\cdot NH_3$		$[X] + Zn \longrightarrow [Y] + Au$
75.	Among the following, which is not the $\pi$ -bonded organo-		Identify $[X]$ and $[Y]$ : $[I.I.T. (S) 2003]$
	metallic compound? [C.B.S.E. (Medical) 2003]		(a) $[X] = [Au(CN)_2]^-, [Y] = [Zn(CN)_4]^{2^-}$
	(a) $(CH_3)_4Sn$ $\Box$ (b) $Cr(\eta^6 - C_6H_6)_2$ $\Box$		(b) $[X] = [Au(CN)_4]^{3-}, [Y] = [Zn(CN)_4]^{2-}$
	(c) $Fe(\eta^5 - C_5H_5)_2$		(c) $[X] = [Au(CN)_2]^-, [Y] = [Zn(CN)_6]^4$
76.	According to the IUPAC nomenclature, sodium nitroprusside		(d) $[X] = [Au(CN)_4]^-, [Y] = [Zn(CN)_6]^{2^-}$
	is named as: [C.B.S.E. (Medical) 2003	07	
,	(a) sodium nitro-ferrocyanide	87.	Which of the following forms with an excess of CN, a
•	(b) sodium pentacyanonitrosyl ferrate (II)		complex having coordination number two?
	(c) sodium nitroferricyanide		[A.I.I.M.S. 2004]
	(d) sodium pentacyanonitrosyl ferrate (III)		(a) $Cu^{2+}$ $\Box$ (b) $Ag^{+}$ $\Box$
77.	The number of unpaired electrons in the complex ion $[CoF_6]^{3-}$		(c) $Ni^{2+}$ $\Box$ (d) $Fe^{2+}$ $\Box$
	is: [C.B.S.E. (Medical) 2003]	88.	Which of the following is not considered as an organo-
	(a) 3		metallic compound? [A.I.I.M.S. 2004]
	(c) 0 $\square$ (d) 2 $\square$		(a) Ferrocene $\Box$ (b) Cis-platin $\Box$
78.	Which of the following octahedral complexes does not show		(c) Zeise's salt $\square$ (d) Grignard reagent $\square$
	geometrical isomerism (A and B are monodentate ligands)?	89.	Which of the following does not have optical isomer?
	[C.B.S.E. (Medical) 2003]		[A.I.I.M.S. 2004]
	(a) $[MA_3B_3]$ $\square$ (b) $[MA_4B_2]$ $\square$		(a) $[Co(en)_3]Cl_3$ $\Box$ (b) $[Co(NH_3)_3Cl_3]$ $\Box$
	(c) $[MA_5B]$ $\Box$ (d) $[MA_2B_4]$ $\Box$	Ì	(c) $[Co(en)_2Cl_2]Cl$ $\Box$ (d) $[Co(en)(NH_3)_2Cl_2]Cl$ $\Box$
79.	The geometry of $[Ni(CN)_4]^2$ and $[NiCl_4]^2$ ions are:	90.	Which of the following is considered to be an anticancer
,,,	[A.F.M.C. 2003]		species? [C.B.S.E. (P.M.T.) 2004]
	(a) tetrahedral		[ CH <sub>2</sub> ]
	(b) square planar		
-	(c) square planar, tetrahedral respectively		(a) $Pt \stackrel{CH_2}{\longrightarrow} Dt \stackrel{CH_2}{\longrightarrow} Dt \stackrel{Cl}{\longrightarrow} Dt \stackrel{Cl}{\longrightarrow} Dt$
	(d) tetrahedral and square planar respectively.		
80.	Complexes with bidentate ligands are called:		[ CI ]
	[Pb. M.E.T. 2003]		
	(a) ligands		(c) $H_3N$ $Pt$ $Cl$ $\Box$ (d) $H_3N$ $Pt$ $Cl$ $\Box$
	(c) complexes $\Box$ (d) none of these $\Box$		$[H_3N]$ $[Cl]$ $NH_3$
	(a) complete (a) notice of most	1	

91.	Among $[Ni(CO)_4]$ , $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ species, the	102. Which of the following will give a pair of enantiomorphs?
	hybridization states of the Ni-atom are respectively:	[C.B.S.E. 2007]
,	[C.B.S.E. (P.M.T.) 2004]	(a) $[Cr(NH_3)_6][Co(CN)_6]$ $\square$ (b) $[Co(en)_2Cl_2]Cl$ $\square$
	(a) $sp^3, dsp^2, dsp^2$ $\Box$ (b) $sp^3, dsp^2, sp^3$ $\Box$	(c) $[Pt(NH_3)_4][PtCl_6]$ $\square$ (d) $[Co(NH_3)_4Cl_2]NO_2$ $\square$
	(a) $sp^3$ , $dsp^2$ , $dsp^2$	103. The d electron configurations of $Cr^{2+}$ , $Mn^{2+}$ , $Fe^{2+}$ and $Ni^{2+}$
92.	Considering H <sub>2</sub> O as a weak-field ligand, the number of	are $3d^4$ , $3d^5$ , $3d^6$ , $3d^8$ respectively. Which of the following
	unpaired electrons in $[Mn(H_2O)_6]^{2+}$ will be:	aqua complexes will exhibit the minimum paramagnetic
	[C.B.S.E. (P.M.T.) 2004]	behaviour? [C.B.S.E. 2007]
		(a) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
	(a) three $\Box$ (b) five $\Box$	
	(c) two	(c) $[Cr(H_2O)_6]^{2+}$
	Which of the following does not have a metal carbon bond?	104. Which of the following statements is not correct?
	(a) $Al(OC_2H_5)_3$ $\Box$ (b) $C_2H_5MgBr$ $\Box$	[P.E.T. (Kerala) 2007]
	(c) $K[Pt(C_2H_4)Cl_3]$ $\square$ (d) $Ni(CO)_4$ $\square$	(a) The complexes [NiCl <sub>4</sub> ] <sup>2-</sup> and [Ni(CN) <sub>4</sub> ] <sup>2-</sup> differ in state
	The correct order of magnetic moments is: [A.I.E.E.E. 2004]	of hybridization of nickel $\Box$
	(a) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]_2^{4-}$	(b) The complexes $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ differ in
	(b) $[MnCl_4]^2 > [Fe(CN)_6]^4 > [CoCl_4]^2$	geometry
	(c) $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$	(c) The complexes [NiCl <sub>4</sub> ] <sup>2-</sup> and [Ni(CN) <sub>4</sub> ] <sup>2-</sup> differ in the
	(d) $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$	magnetic properties
95.	Coordination compounds have great importance in biological	(d) The complexes [NiCl <sub>4</sub> ] <sup>2-</sup> and [Ni(CN) <sub>4</sub> ] <sup>2-</sup> differ in primary
	systems. In this context which of the following statements	valencies of nickel
	is incorrect? [A.I.E.E.E. 2004]	(e) Nickel ion has the same secondary valency in the
	(a) Chlorophyll is a green pigment in plants and contains	complexes $[NiCl_4]^2$ and $[Ni(CN)_4]^2$
	calcium	105. Both Co <sup>3+</sup> and Pt <sup>4+</sup> have a coordination number of 6. Which
	(b) Haemoglobin is the red pigment of blood and contains	of the following pairs of complexes will show approximately
	iron $\square$	the same electrical conductance for their 0.001M aqueous
	(c) Cyanocobalamin is $B_{12}$ and contains cobalt	solutions? [P.E.T. (Kerala) 2007]
	(d) Carboxypeptidase $A$ is an enzyme and contains zinc $\square$	(a) $CoCl_3\cdot 4NH_3$ and $PtCl_4\cdot 4NH_3$
96.	Which one of the following complexes is an outer orbital	(b) $CoCl_3 \cdot 3NH_3$ and $PtCl_4 \cdot 5NH_3$
	complex? [A.J.E.E.E 2004]	(c) $CoCl_3 \cdot 6NH_3$ and $PtCl_4 \cdot 5NH_3$
	(a) $[Fe(CN)_6]^{4-}$	(d) $CoCl_3$ ·6NH <sub>3</sub> and $PtCl_4$ ·3NH <sub>3</sub>
	(a) $[Fe(CN)_6]^{4-}$	(e) $CoCl_3 \cdot 5NH_3$ and $PtCl_4 \cdot 6NH_3$
97.	Which one is an organometallic compound?	106. Facial-meridional isomerism is associated with which one of
	[M.P. (P.E.T.) 2004]	the following complexes? [M = central metal.]
	(a) Lithium acetate	[P.M.T. (Kerala) 2007]
	(b) Lithium methoxide	(a) $[M(AA)_2]$ $\Box$ (b) $[MA_3B_3]$ $\Box$
	(c) Lithium dimethylamide	(c) $[M(AA)_3]$ $\square$ (d) $[MABCD]$ $\square$
-	(d) Methyl lithium	(e) $[MA_4B_2]$
98.	The species having tetrahedral shape is: [I.I.T. 2004;	107. The increasing order of the crystal field splitting power of
	A.I.I.M.S. 2007]	some common ligands is: [P.M.T. (Kerala) 2007]
	(a) $[PdCl_4]^2$	(a) $H_2O < OH^- < CI^- < F^- < CN^-$
	(c) $[Pd(CN)_4]^2$ $\Box$ (d) $[NiCl_4]^2$ $\Box$	(b) $H_2O < Cl^- < OH^- < CN^- < F^-$
99.	Which one of the following complexes will have four	(c) $CN^- < H_2O < OH^- < F^- < CI^-$
	isomers?	(d) $F^- < CN^- < OH^- < CI^- < H_2O$
	(a) $[Co(en)(NH_3)_2Cl_2]Cl$	(e) $Cl^- < F^- < OH^- < H_2O < CN^-$
	(b) [Co(PPh <sub>3</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]Cl	108. Which one of the following is a tridentate ligand?
	(c) [Co(en) <sub>3</sub> ]Cl <sub>3</sub>	[P.M.T. (Kerala) 2007]
	(d) $[\operatorname{Co(en)}_2\operatorname{Cl}_2]\operatorname{Br}$	(a) $NO_2^-$
100.	Which of the following shall form an octahedral complex?	(c) Glycinate ion
ä.	(a) $d^4$ (low spin) $\Box$ (b) $d^8$ (high spin) $\Box$	(e) EDTA □
	(c) $d^6$ (low spin) $\Box$ (d) All of these $\Box$	109. The dark blue colour of the solution formed when excess of
101.	Which of the following has a square planar geometry?	ammonia is added to a solution of copper(II) sulphate is due
	[A,I,E,E,E, 2007]	to the presence of the ion: [P.M.T. (Kerala) 2007]
٠	(a) $[PtCl_4]^{2-}$	(a) $[Cu(OH)_4(H_2O)_2]^{2+}$ $\Box$ (b) $[Cu(H_2O)_6]^{2+}$ $\Box$
	(c) $[FeCl_4]^2$ $\Box$ (d) $[NiCl_4]^2$ $\Box$	(c) $[Cu(NH_4)_2(H_2O)_4]^{4+} \square$ (d) $[Cu(NH_3)_2(H_2O)_4]^{2+} \square$
	(4) [1 (4) [1 (4)]	(4) [04(14,7)/2(4,72)/4]

[Hint: The formula of the complex is  $[M(H_2O)_4Cl_2]Cl$ .  $0.1 \times V = 0.01 \times 200$ V = 20 1

		•								
110.	$CoCl_3xNH_3$ , one mole of A of $x$ ?		in excess to 1M solution of is formed. What is the value [E.A.M.C.E.T. (Med.) 200	ie						
111.	(a) 1 [c) 3 [d] Assign the hybridization, K <sub>2</sub> [Cu(CN) <sub>4</sub> ]: (a) $sp^3$ , tetrahedral, 1.73 B. (b) $dsp^2$ , square planar, 1.7	⊐ sha M.	(b) 2 [ (d) 4 [ pe and magnetic moment of [J.E.E. (Orissa) 200							
112.	(c) $sp^3$ , tetrahedral, 2.44 B. (d) $dsp^2$ , square planar, 2.4 Octahedral complex, $a \qquad b$	M.	I							
	a $b$ is:		[D.C.E. (Engg.) 200	7]						
	(a) cis		(h) trans	_						
			(b) trans (d) fac							
112	(-)		are diamagnetic. The hybrid	-						
115.	sations of nickel in these			п-						
	sations of mekel in these c	OIII	piexes, respectively, are: [1.1.T. 200]	Q1						
	(a) $\operatorname{cn}^3 \operatorname{cn}^3$	П	(b) $en^3 den^2$	[0]						
	(a) $sp^3$ , $sp^3$ (c) $dsp^2$ , $sp^3$		(b) $sp^3$ , $dsp^2$ (d) $dsp^2$ , $dsp^2$	7						
114				81						
117.	The IUPAC name of [Ni(NH <sub>3</sub> ) <sub>4</sub> ] [NiCl <sub>4</sub> ] is : [1.1.T. 2008] (a) tetrachloronickel(II)-tetraamminenickel (II)									
	(b) tetraamminenickel (II)-									
	(c) tetraamminenickel (II)-									
	(d) tetrachloronickel (II)-te			$\overline{\Box}$						
115	* *		nplexes exhibits the higher	est						
115.	paramagnetic behaviour?	001	[C.B.S.E. 200							
		П	(b) $[Ti(NH_3)_6]^{3+}$	n						
			(d) $[Fe(en)(bpy)(NH_3)_2]^{2+}$	$\exists$						
116			lination entities, the magnitu	de						
	of $\Delta_0$ [CFSE in octahedral is									
			C.B.S.E. 2008; A.I.E.E.E. 200	180						
	(a) [Co(CN) <sub>6</sub> ] <sup>3-</sup>									
	(a) $[Co(CN)_6]^{3-}$ (c) $[Co(H_2O)_6]^{3+}$		(b) $[Co(C_2O_4)_3]^{3-}$ (d) $[Co(NH_3)_6]^{3+}$							
117			ons calculated in [Co(NH <sub>3</sub> ) <sub>6</sub> ]	3+						
	and $[CoF_6]^{3-}$ are:		[V.I.T.E.E.E. 200	1						
	(a) 4 and 4		(b) 0 and 2	ď						
	(c) 2 and 4		(d) 0 and 4							
118	_	ą sa	It containing Zn <sup>2+</sup> ion is:	ļ						
			· [V.I.T.E.E.E. 200	18]						
	(a) 0		(b) 1.87							
	(c) 5.92		(d) 2							
119			valencies of chromium in t							
		xala	tochromium (III), are respe							
	tively:		[P.E.T. (Kerala) 200							
	(a) 3,4	닏	(b) 4,3							
100	(c) 3,6	Ш	(d) 6,3							

[J.E.E. (Orissa) 2008]

is:

126.	Out of $TiF_6^{2-}$ , $CoF_6^{3-}$ , $Cu_2Cl_2$ and $NiCl_4^{2-}$ , the colourless	(a) $[CoCl(NH_3)_5]Cl_2$ $\Box$ (b) $[Co(NH_3)_6]Cl_3$ $\Box$
	species are: [C.B.S.E. (P.M.T.) 2009]	(c) $[Co(NH_3)_4Cl_2]Cl$ $\Box$ (d) $[Co(NH_3)_3Cl_3]$ $\Box$
	(a) $Cu_2Cl_2$ and $NiCl_4^{2-}$ $\square$ (b) $TiF_6^{2-}$ and $Cu_2Cl_2$ $\square$	[Hint: Number of moles of complex = $\frac{2.675}{2675}$ = 0.01
	(c) $CoF_6^{3-}$ and $NiCl_4^{2-}$ $\square$ (d) $TiF_6^{2-}$ and $CoF_6^{3-}$ $\square$	
	[Fint: In TiF <sub>6</sub> <sup>2</sup> , Ti <sup>4+</sup> : $3d^0$ , colourless; In CoF <sub>6</sub> <sup>3-</sup> , Co <sup>3+</sup> : $3d^6$ ,	Number of moles of AgCl = $\frac{4.78}{1435}$ = 0.03
	coloured; In Cu <sub>2</sub> Cl <sub>2</sub> , Cu <sup>+</sup> : 3d <sup>10</sup> , colourless; In NiCl <sub>4</sub> <sup>2-</sup> ,	This shows that three Cl ions are ionisable in the
	$Ni^{2+}: 3d^8$ , coloured.]	complex.]
127.	Which of the following does not show optical isomerism?	136. Which one of the following complexes is not expected to
	[C.B.S.E. (P.M.T.) 2009]	exhibit isomerism? [C.B.S.E. (P.M.T.) 2010]
	(a) $[Co(NH_3)_3Cl_3]$ $\Box$ (b) $[Co(en)Cl_2(NH_3)_2]^+$ $\Box$	(a) $[Ni(NH_3)_4(H_2O)_2]^{2+} \square$ (b) $[Pt(NH_3)_2Cl_2] \square$
	(c) $[\text{Co(en)}_3]^{3+}$	(c) $[Ni(NH_3)_2Cl_2]$ $\Box$ (d) $[Ni(en)_3]^{2+}$ $\Box$
128	Which of the following complex ion is expected to absorb	137. The ionization isomer of [Cr(H <sub>2</sub> O) <sub>4</sub> ClNO <sub>2</sub> ]Cl is: [LLT. 2010]
. 120,	visible light? [C.B.S.E. (P.M.T.) 2009]	(a) $[Cr(H_2O)_4NO_2]Cl_2$
	(a) $[\text{Ti}(\text{en})_2(\text{NH}_3)_2]^{4+}$ $\Box$ (b) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ $\Box$	(c) $[Cr(H_2O)_4Cl(ONO)]Cl \square$ (d) $[Cr(H_2O)_4Cl_2NO_2]H_2O \square$ 138. The complex showing a spin-only magnetic moment of 2.82
	2	B.M. is: [I.T. 2010]
100		(a) Ni(CO) <sub>4</sub> $\Box$ (b) [NiCl <sub>4</sub> ] <sup>2-</sup> $\Box$
129.	The compound(s) that exhibit(s) geometrical isomerism is(are): [I.I.T. 2009]	(a) Ni(CO) <sub>4</sub> $\square$ (b) [NiCl <sub>4</sub> ] <sup>2-</sup> $\square$ (c) Ni(PPh <sub>3</sub> ) <sub>4</sub> $\square$ (d) [Ni(CN) <sub>4</sub> ] <sup>2-</sup> $\square$
	• •	[Hint: $Ni^{2+}$ undergoes $sp^{3}$ -hybridization and there are two
	(a) $[Pt(en)Cl_2]$ $\square$ (b) $[Pt(en)_2]Cl_2$ $\square$	unpaired electrons in $3d$ -orbital in the complex $[NiCl_4]^{2-}$
	(c) $[Pt(en)_2Cl_2]Cl_2$ $\square$ (d) $[Pt(NH_3)_2Cl_2]$ $\square$	as chlorine is a weak ligand.]
130.	Which of the following has an optical isomer?	139. Which of the following complex ions is not expected to
	[A.I.E.E.2009]	absorb visible light? [C.B.S.E. (P.M.T.) 2010]
	(a) $[Co(NH_3)_3CI]^+$	(a) $[Ni(CN)_4]^{2-}$
	(c) $[Co(H_2O)_4(en)]^{3+}$	(c) $[Fe(H_2O)_6]^{2+}$
131.	Which of the following pairs represent linkage isomers?	140. Which of the following is an outer orbital complex?
	[A.I.E.E.E. 2009]	[A.M.U. (Engg.) 2010]
	(a) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$	(a) $[Cr(NH_3)_6]^{3+}$
	(b) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$	(c) $[Fe(CN)_6]^{3-}$ $\Box$ (d) $[Mn(CN)_6]^{4-}$ $\Box$
	(c) $[Co(NH_3)_5(NO_3)]SO_4$ and $[Co(NH_3)_5(SO_4)]NO_3$	141. Which complex of Co <sup>2+</sup> will have the weakest crystal field
	(d) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$	splitting? [A.M.U. (Engg.) 2010]
132.	In Cu-ammonia complex, the state of hybridisation of Cu <sup>2+</sup>	(a) $[Co(CN)_6]^4$
	is: [J.E.E. (WB) 2009]	(c) $[Co(en)_3]^{2+}$
	(a) $sp^3$ $\Box$ (b) $d^3s$ $\Box$	142. Which among the following statements are true for the
	(c) $sp^2f$ $\Box$ (d) $dsp^2$ $\Box$	complex, [Co(NH <sub>3</sub> ) <sub>6</sub> ][Cr(CN) <sub>6</sub> ]? [P.E.T. (Kerala) 2010]
133.	The oxidation state of iron in the brown ring complex	1. It is a non electrolyte.
	[Fe(H2O)5NO]SO4 is: [C.E.T. (Karnataka) 2009]	2. The magnitude of the charge on each complex ion is 3.
	(a) $0 \qquad \square \qquad (b) + 2 \qquad \square$	3. The complex will not conduct current.
	(c) +1	4. The complex will exhibit coordination isomerism.
134.	Which one of the following has an optical isomer?	5. The magnitude of the charge on each complex ion is 1.
	[A.LE.E. 2010]	[P.E.T. (Kerala) 2010]
	(a) $[Zn(en)_2]^{2+}$ $\Box$ (b) $[Zn(en)(NH_3)_2]^{2+}$ $\Box$	(a) 1 and 4
105	(c) $[Co(en)_3]^{3+}$ $\square$ (d) $[Co(H_2O)_4(en)]^{3+}$ $\square$	(c) 1 and 3
135	A solution contains 2.675 g of CoCl <sub>3</sub> ·6NH <sub>3</sub> (molar mass	(e) 2 and 4
	= 267.5 g mol <sup>-1</sup> ) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess	143. An example of ambidentate ligand is: [P.E.T. (Kerala) 2010]  (a) Ammine   (b) Aquo
,	of AgNO <sub>3</sub> to give 4.78 g of AgCl. The formula of the complex	(c) Chloro
.,	is: [A.L.E.E. 2010]	(e) Thiocyanato
	10.	

H	nsw	ers																	
1.	(b)	2.	(c)	3.	(c)	4.	(d)	5.	(a)	6.	(a)	7.	(d) .	8.	(b)	9.	(a)	10.	(b)
11.	(d)	12.	(d)	13.	(c)	14.	(c)	15.	(a)	16.	(b)	17.	(d)	18.	(d)	19.	(a)	20.	(d)
21.	(c)	22.	(c)	23.	(b)	24.	(b)	25.	(b)	26.	(c)	27.	(a)	28.	(d)	29.	(c)	30.	(b)
31.	(b)	32.	(b)	33.	(c)	34.	(c)	35.	(c)	36.	(a)	37.	(a)	38.	(d)	39.	(d)	40.	(a)
41.	(d)	42.	(a)	43.	(d)	44.	(b)	45.	(d)	46.	(b)	47.	(c)	48.	(c) and (d)	49.	(a)	50.	(a)
51.	(b)	52.	(b)	53.	(c)	54.	(b)	55.	(c)	56.	(b)	57.	(a)	58.	(b)	59.	(a)	60.	(d)
61.	(b)	62.	(b)	63.	(a)	64.	(d)	65.	(a)	66.	(d)	67.	(a)	68.	(b)	69.	(d)	70.	(a)
71.	(b)	72.	(b)	73.	(b)	74.	(a)	75.	(a)	76.	(b)	77.	(b)	78.	(c)	79.	(c)	80.	(b)
81.	(b)	82.	(a)	83.	(a)	84.	(b)	85.	(a)	86.	(a)	87.	(b)	88.	(b) ·	89.	(b) ·	90.	(c)
91.	(b)	92.	(b)	93.	(a)	94.	(a)	95.	(a)	96.	(d)	97.	(d)	98.	(d)	99.	(d)	100.	(d)
101.	(a)	102.	(b)	103.	(b)	104.	(d)	105.	(c)	106.	(b)	107.	(e)	108.	(d)	109.	(e)	110.	(d)
111.	(b)	112.	(d)	113.	(b)	114.	(c)	115.	(d)	116.	(a)	117.	(d)	118.	(a)	119.	(c)	120.	(b)
121	(a)	122.	(d)	123.	(b)	124.	(c)	125.	(b)	126.	(b)	127.	(a)	128.	(b)	129.	(c, d)	130.	(d)
131.	(b)	132.	(d)	133.	(c)	134.	(c)	135.	(b)	136.	(c)	137.	(b)	138.	(b)	139.	-(a)	140.	_(b)
	(b) •	142.	(e)	143.					•			***		,			,	·	

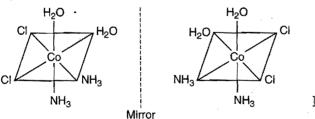


# **Objective Questions for IIT ASPIRANTS**

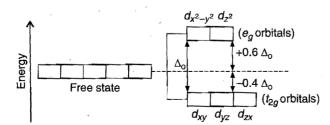


- The coordination number and oxidation number of M in the complex, [M(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]Cl are:
  - (a) 10,3
- (b) 6,4
- (c) 2, 6
- (d) 6.3
- 2. CuSO<sub>4</sub>·5H<sub>2</sub>O is a coordination compound. It can be represented as:
  - (a)  $[Cu(H_2O)_4]SO_4 \cdot H_2O$
- (b) [Cu(H<sub>2</sub>O)<sub>3</sub>]SO<sub>4</sub>·2H<sub>2</sub>O
- (c)  $[Cu(H_2O)_2]SO_4:3H_2O$
- (d)  $[Cu(H_2O)_5]SO_4$
- The complex/complex ion, which shows optical activity is:
  - (a) [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>]<sup>†</sup>
- (b) [Co(H<sub>2</sub>O)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>
- (c) [Co(NH<sub>3</sub>)<sub>6</sub>]
- (d) [Co(CN)5NC]

[Hint:



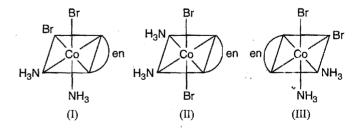
4.



The above splitting of d-orbitals takes place in the formation of:

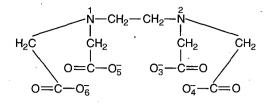
- (a) tetrahedral complexes
- (b) square-planar complexes

- (c) octahedral complexes
- (d) both tetrahedral and square-planar complexes
- 5. Which of the following pairs of complexes are isomeric with each other but their aqueous solutions exhibit different molar conductivities?
  - (a)  $[PtCl_2(NH_3)_4] Br_2$ and [Pt(NH<sub>3</sub>)<sub>4</sub>Br<sub>2</sub>] Cl<sub>2</sub>
  - (b) [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>] NO<sub>2</sub> [Co(NH<sub>3</sub>)<sub>4</sub>CINO<sub>2</sub>] CI and
  - [Co(NH<sub>3</sub>)<sub>5</sub>ONO] Cl<sub>2</sub> (c)  $[Co(NH_3)_5NO_2]Cl_2$ and
  - [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>] Br (d) [Co(NH<sub>3</sub>)<sub>5</sub>Br] SO<sub>4</sub> and
  - [Hint: They are ionisation isomers but their molar conductivities are different due to different magnitude of charge on the cation and anion.]
- Three arrangements are shown for the complex, [Co(en)(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup>. Which one is the wrong statement?



- (a) I and II are geometrical isomers
- (b) II and III are optical isomers
- (c) I and III are optical isomers
- (d) II and III are geometrical isomers
- 7. The donor sites of EDTA ligand are:
  - (a) O atoms only
  - (b) N atoms only
  - (c) two N atoms and four O atoms
  - (d) three N atoms and three O atoms

[Hint: The structure of EDTA ion is:



1, 2 are donor N atoms and 3, 4, 5, 6 are donor O atoms.]

- **8.** Which of the following can act as ligand but does not have any lone or unshared pair of electrons?
  - (a)  $C_2H_4$

(b) NH<sub>3</sub>

(c) H<sub>2</sub>O

(d) Cl<sup>-</sup>

[Hint:  $C_2H_4$  does not possess an unshared lone pair but it can act as  $\pi$ -acid ligand.]

9. A complex is prepared by mixing CoCl<sub>3</sub> and NH<sub>3</sub>. 0.1 *M* solution of the complex was found to freeze at -0.372°C. The formula of the complex is:

[Molal depression constant of water = 1.86°C/m]

- (a) [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub>
- (b) [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>
- (c) [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl
- (d)  $[Co(NH_3)_3Cl_3]$

[Hint:

 $\Delta T_f = i \times K_f \times m = i \times 1.86 \times 0.1$ 

or  $0.372 = 0.186 \times i$ 

or i = 2

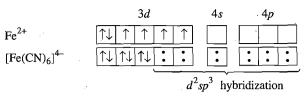
This shows that the complex gives two ions in solution. Thus, the formula of the complex is  $[Co(NH_3)_4Cl_2]Cl$ .  $[Co(NH_3)_4Cl_2]$   $Cl \rightleftharpoons [Co(NH_3)_4Cl_2]^+ + Cl^-$ 

- 10. Which statement is wrong?
  - (a) All the octahedral complexes of Ni<sup>2+</sup> are outer orbital complexes
  - (b) (SCN) shows linkage isomerism in coordination compounds
  - (c) All ligands are Lewis bases
  - (d) NH<sub>4</sub> ion can act as a ligand

[Hint: NH<sub>4</sub><sup>+</sup> ion does not act as ligand because nitrogen atom has no lone pair of electrons which it can donate to metal atom.]

- 11. Which of the following is correct?
  - (a) The IUPAC name of Mn<sub>3</sub>(CO)<sub>12</sub> is dodecacarbonyl trimanganese (0)
  - (b) The IUPAC name of  $K[BF_4]$  is tetrafluoroboron potassium (I)
  - (c) The IUPAC name of  $K_3[Al(C_2O_4)_3]$  is potassium trioxalate aluminium (III)
  - (d) The IUPAC name of K<sub>4</sub>[Fe(CN)<sub>6</sub>] is potassium ferrocyanide
- 12. Which of the following is not correct?
  - (a)  $[Fe(CN)_6]^{3-}$  is weakly paramagnetic
  - (b) [Fe(CN)<sub>6</sub>]<sup>4</sup> is strongly paramagnetic
  - (c) [Ni(CN)<sub>4</sub>]<sup>2-</sup> is diamagnetic
  - (d) [NiCl<sub>4</sub>]<sup>2-</sup> is paramagnetic

[Hint:  $[Fe(CN)_6]^4$  involves  $d^2sp^3$  hybridization. As CN<sup>-</sup> is a strong ligand, the pairing of electrons occurs, thus, it is a diamagnetic ion.



All orbitals are doubly occupied.]

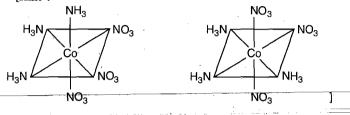
- 13. The number of geometrical isomers of  $[Co(NH_3)_3(NO_3)_3]$  are:
  - (a) 0

(b) 2

(c) 3

(d) 4

Hint:



Cis-form

Trans-form

- 14. The complex ion which has no d electron in the central metal atom is: [At. No. Cr = 24, Mn = 25, Fe = 26, Co = 27]
  - (a)  $MnO_4$
- (b)  $[Co(NH_3)_6]^{34}$
- (c)  $[Fe(CN)_6]^{3-}$
- (d)  $[Cr(H_2O)_6]^{3+}$
- **15.** In  $[Cr(C_2O_4)_3]^{3-}$ , the isomerism shown is :
  - (a) ligand
- (b) geometrical
- (c) optical
- (d) ionisation
- **16.**  $[Fe(H_2O)_6]^{2+}$  and  $[Fe(CN)_6]^{4-}$  differ in :
  - (a) geometry, magnetic moment
    - (b) magnetic moment, colour
    - (c) geometry, hybridization
    - (d) hybridization, number of unpaired electrons

[Hint:  $[Fe(H_2O)_6]^{2+}$  is paramagnetic while  $[Fe(CN)_6]^{4-}$  is diamagnetic.  $[Fe(H_2O)_6]^{2+}$  has pale green colour while  $[Fe(CN)_6]^{4-}$  has yellow colour.]

- 17. Complexes formed in the following methods are:
  - (i) cyanide process for extraction of silver
  - (ii) Mond's process for extraction of nickel
  - (iii) photographic fixing process
  - (iv) removal of Ca<sup>2+</sup> ions from hard water by EDTA.

- **18.** Which of the following statements is not correct?
  - (a) Higher the charge density on the central ion, the greater is the stability of its complexes
  - (b) Chelating ligands form more stable complexes as compared to monodentate ligands
  - (c) The higher the oxidation state of the metal, the more stable is the complex
  - (d) The cyano and ammine complexes are less stable than those formed by halide ions

- 19. Match the correct organic ligands used for the estimation of Ni<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> ions.
  - (i) Dimethyl glyoxime
- (ii) 1, 10-phenanthroline
- (iii) 8-hydroxy quinoline
  - (I)
- (III)
- $A1^{3+}$ (a) (b)
- Ni<sup>2+</sup> A1<sup>3+</sup>

- (c)
- A1<sup>3+</sup>
- Fe<sup>3+</sup> (d)
- Ni<sup>2+</sup>
- The EAN of a metal carbonyl,  $M(CO)_r$  is 36. The atomic number of metal is 24. The value of x is :
  - (a) 6

(c) 4

(d) 3

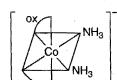
[Hint: EAN =  $36 = 2 \times x + 24$ ]

- **21.** *M*—*L* bonds in carbonyl possess :
  - (a) only sigma character
  - (b) only  $pi(\pi)$  character
  - (c) both sigma ( $\sigma$ ) and pi ( $\pi$ ) characters
  - (d) none of the above
- 22. The number of possible isomers of an octahedral complex,  $[Co(C_2O_4)_2(NH_3)_2]^{-1}$  is:
  - (a) 1

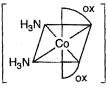
(b) 2

(c) 3

- (d) 4
- [Hint:

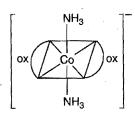






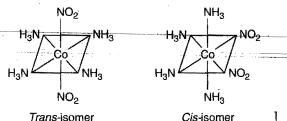
Cis-d-isomer

Cis-I-isomer



Trans-isomer

- 23.  $[Co(NH_3)_4(NO_2)_2]Cl$  exhibits:
  - (a) ionisation isomerism, geometrical isomerism and optical isomerism
  - (b) linkage isomerism, geometrical isomerism and optical isomerism
  - (c) linkage isomerism, ionisation isomerism and optical isomerism
  - (d) linkage isomerism, geometrical isomerism and ionisation isomerism
  - [Hint: (i) NO<sub>2</sub> is an ambidentate group. It can show linkage isomerism.
    - (ii) The complex can show ionisation isomerism with the complex [Co(NH<sub>3</sub>)<sub>4</sub>NO<sub>2</sub>Cl] NO<sub>2</sub>.
    - (iii) The complex shows geometrical isomerism.



Trans-isomer

Cis-isomer

- 24. When excess of ammonia is added to copper sulphate solution, the deep blue coloured complex is formed. The complex is:
  - (a) tetrahedral, paramagnetic
  - (b) tetrahedral, diamagnetic
  - (c) square planar, diamagnetic
  - (d) square planar, paramagnetic
  - [Hint:  $[Cu(NH_3)_4]^{2+}$  complex is formed by  $dsp^2$  hybridization and one electron is shifted to 4p-orbital.

 $dsp^2$ (square planar)]

1. (d) 2. (a) 3. (b) 4. (c) 5. (d) 6. (b) 7. (c) 8. (a) 9. (c) 10. (d) 11. (a) 12. (b) 17. (b) 22. (c) 13. (b) 14. (a) 15. (c) **16.** (b) 18. (d) 19. (c) 20. (a) 21. (c) 23. (d) 24. (d)

# Matrix Matching Questions for IIT Aspirants

## Coordination Compounds and Organometallic Compounds

Match the compounds in List-I with their classification in List-II:

### List-I

#### List-II

(a) LiAlH<sub>4</sub>

- (p) Reducing agent
- (b) KClMgCl2·6H2O
- (q) Double salt
- (c)  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
- (r) Alum
- (d) NaBH<sub>4</sub>

- (s) Complex hydride
- 2. Match the ligands in List-I with their classification in List-II:

#### List-I

#### List-II

(a) EDTA

(p) Monodentate

(b) DMG

- (q) Chelate ligand
- (c) Ethylenediammine (d) CN----
- (r) Bidentate (s) Hexadentate
- Match the complexes in List-I with their informations in List-II:

### List-I

#### List-II

- (a)  $[Cu(NH_3)_4]SO_4$
- (p)  $dsp^2$
- (b)  $[Pt(NH_3)_2Cl_2]$ (c)  $K_4[Fe(CN)_6]$
- (q) Octahedral (r)  $sp^3d^2$
- (d) [Fe(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>
- (s) Square planar
- 4. Match List-I with List-II: List-T

### List-II

- (a)  $d^2 s p^3$
- (p) Outer orbital octahedral complex
- (b)  $sp^{3}d^{2}$
- (q) High spin complex (r) Low spin complex
- (c) K<sub>3</sub>[Fe(CN)<sub>6</sub>] (d) [Fe(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>
- (s) Inner orbital octahedral complex
- 5. Match List-II with List-II: List-I

- (a) Ferrocene
- (b)  $Mn_2(CO)_{10}$
- (c) Vitamin B<sub>12</sub>
- (d) Heme

- List-II
- (p) Iron present
- (g) Cobalt -
- (r) Metal-metal bonding
- (s) Sandwich structure

6. Match List-II with List-II:

#### List-I

### List-II

- (a)  $[MnCl_6]^{2-}$
- (p) One unpaired electron
- (b)  $[Fe(CN)_6]^{3-}$
- (q)  $d^2sp^3$
- (c)  $[CoF_6]^{3-}$
- (r)  $sp^3d^2$
- (d)  $[Fe(H_2O)_6]^{2+}$
- (s) Four unpaired electrons
- 7. Match the complexes in the List-I with their coordination number in the List-II:

#### List-I

#### List-II

- (a)  $[Co(en)_3]^{3+}$
- (b)  $[Ca(EDTA)]^{2-}$
- (p) 6(q) 4
- (c) [Ni(CO)<sub>4</sub>]

- (r) 2
- (d) [Ag(NH<sub>3</sub>)<sub>2</sub>]Cl

- (e) [Fe(CO)<sub>5</sub>]
- Match the hybridization in List-I with its inference in complex
- compounds List-II:

### List-I

### List-II

(a) sp (b)  $sp^3$  (p) Octahedral (q) Tetrahedral

(c)  $sp^3d^2$ 

(r) Linear

(d)  $d^2sp^3$ 

- (s) Do not show geometrical
- isomerism Match the complexes in List-I with their stereoproperties in
- List-II:

### List-I

### (p) Show facial form

- (a)  $[CoCl_3(NH_3)_3]$ (b)  $[Cr(OX)_3]^{3-}$
- (q) Cis form is optically active

List-II

- (c)  $[CrCl_2(OX)_2]$
- (r) Trans form is optically inactive
- (d)  $[RhCl_3(Py)_3]$
- (s) Show meridian form
- Match the complexes in List-I with their properties listed in List-II: [I.LT. 2007]

#### List-I

### List-II

- (a)  $[Co(NH_3)_4(H_2O)_2]Cl_2$
- (b)  $[Pt(NH_3)_2Cl_2]$
- (p) Geometrical isomers (q) Paramagnetic
- (c) [Co(H<sub>2</sub>O)<sub>5</sub>Cl]Cl
- (r) Diamagnetic
- (d)  $[Ni(H_2O)_6]Cl_2$
- (s) Metal ion with +2 oxidation state

(a-p, s)

(a-p, s)

- (b-q) (c-q, r) (a-q, s)(b-q, r)(c-q, r)
- (a-r, s) (b-p, q)
  - (b-r)

(b-p, s)

(c-r, s) (c-q)

(c-q)

(d-p, q)(d-p)

(d-p, s)

(d-q, r)

(d-p)

- (a-p, q) (a-p)
- (b-p, q)(b-p)
- (c-r, s) (c-q)
- (d-r, s)(d-r)(d-p)
- -(e-s)
- (a-r, s) (b-q, s)(c-p) (a-p, s)(b-q, r) (c-q, r)
- **10.** (a-p, q, s) (b-p, r, s)
- (d-p, s)
  - (c-q, s)(d-q, s)

# **Assertion-Reason Type Questions**

The questions given below consist of Assertion (A) and **Reason** (R). Use the following key to select the correct answer:

- (a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
- (b) If both (A) and (R) are correct but (R) is not correct explanation for (A).
- (c) If (A) is correct but (R) is incorrect.
- (d) If both (A) and (R) are incorrect.
- (e) If (A) is incorrect but (R) is correct.
- 1. (A) [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>] does not give a white precipitate with AgNO<sub>3</sub> solution.
  - (R) Chlorine is not present in the ionising sphere.
- (A) The ligands, thiocyanato (SCN) and isothiocyanato (NCS<sup>-</sup>) are ambidentate.
  - (R) The ligands form linkage isomers.
- (A) Ni(CO)<sub>4</sub> is diamagnetic in nature.
  - (R) Ni-atom undergoes  $sp^3$  hybridization.
- (A) Cis-isomer of [Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl shows optical activity.
  - (R) Cis-isomer of [Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl is a symmetric molecule.
- 5. (A) Complexes containing three bidentate groups such as  $[Cr(ox)_3]^{3-}$  and  $[Co(en)_3]^{3+}$  do not show optical activity.
  - (R) Octahedral complex, [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl shows geometrical isomerism.
- 6. (A) Tetrahedral complexes do not show geometrical iso-
  - (R) The relative positions of the ligands in the tetrahedral complex are the same w.r.t. each other.
- 7. (A) Ti(OC<sub>6</sub>H<sub>5</sub>)<sub>4</sub> is an organometallic compound.
  - (R) Acetate ion can form a chelate.
- (A) EAN of Cr in its complexes is always 36.
  - (R) Oxidation state of Cr in Cr(CO)<sub>6</sub> is zero.
- (A)  $K_3[Fe(CN)_6]$  is a low spin complex.
  - (R) Fe<sup>2+</sup> ion in this complex undergoes  $sp^3d^2$  hybridization.
- 10. (A) Coordination isomerism occurs when both cation and anion are complex.
  - (R) The complexes with coordination number 6 form octahedral complexes involving either  $sp^3d^2$  or  $d^2sp^3$ hybridization.

- 11. (A) Metals possess two types of valencies-primary and secondary. The primary valency is not ionisable while secondary valency is ionisable.
  - (R) The IUPAC name of K<sub>3</sub>[Fe(CN)<sub>6</sub>] is potassium ferricyanide.
- 12. (A) After splitting of d-orbitals during complex formation, the orbitals form two sets of orbitals  $t_{2p}$  and  $e_p$ .
  - (R) Splitting of d-orbitals occurs only in the case of strong field ligands such as CN-.
- 13. (A) Ferrocene is a  $\pi$ -bonded complex.
  - (R) All organometallic compounds are  $\pi$ -bonded complexes.
- 14. (A) All inner orbital complexes are diamagnetic.
  - (R) Inner orbital complexes contain only paired orbitals.
- 15. (A) Organometallic compounds are those which have one or more metal-carbon bonds.
  - (R) Metallic carbonyls are organometallic compounds having both  $\sigma$  and  $\pi$ -bonds.
- **16.** (A) In octahedral complexes, the three orbitals  $(d_{xy}, d_{yz}, d_{zx})$ are stable and of low energy while the two orbitals  $(d_{x^2-v^2}, d_{z^2})$  are unstable and have high energy.
  - (R) In octahedral complexes, the three d-orbitals  $(d_{xy}, d_{yz}, d_{zx})$ experience less repulsion from the ligands while two d-orbitals  $(d_{x^2-y^2}, d_{z^2})$  experience more repulsion from the ligands due to their shapes.
- 17. (A)  $[Co(NO_2)_3(NH_3)_3]$  does not show optical isomerism.
  - (R) It has a plane of symmetry.
- **18.** (A)  $[Fe(H_2O)_5NO]SO_4$  is paramagnetic.
  - (R) The Fe in [Fe(H<sub>2</sub>O)<sub>5</sub>NO]SO<sub>4</sub> has three unpaired electrons.

[Hint: Fe<sup>+</sup>-one electron from 4s is shifted to 3d i.e., it has  $3d^7$  configuration.

3 unpaired electrons]

- 19. (A) The geometrical isomers of the complex  $[M(NH_3)_4Cl_2]$  are optically inactive.
  - (R) Both geometrical isomers of the complex  $[M(NH_3)_4Cl_2]$ possess axis of symmetry.

1. (a)

2. (a)

3. (b)

4. (c)

**5.** (e)

**6.** (a)

7. (d)

**8.** (e)

(c)

10. (b)

12. (c) 13. (c) 14. (d) 15. (b) 16. (a) 17. (a) 18. (a) 11. (d) 19. (a)

# **HOUGHT TYPE QUESTIONS**



### THOUGHT 1

The neutral molecules, anions or cations which are directly linked with a central metal atom or ion in a complex are called ligands. A ligand is a species that is capable of donating an electron pair or pairs to the central metal atom or ion. It acts as a Lewis base. The ligands having two or more donor atoms are called polydentate or multidentate ligands. A multidentate ligand is known as a chelating ligand if on coordination it results in formation of a closed or cyclic ring. The complexes, thus, formed are known as chelates. Chelates are usually more stable.

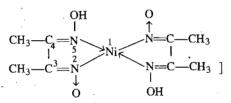
- 1. Which of the following ligands can form chelates?
  - (a) Ethylenediamine
- (b) Oxalic acid
- (c) Glycine
- (d) All of these
- How many donor sites are present in ethylenediamine tetraacetate ligand?
  - (a) 2

(b) 3

(c) 4

- (d) 6
- 3. Ni<sup>2+</sup> ion forms a scarlet red complex with DMG. It is a . . . . ... membered closed ring structure.
  - (a) 3
- (b) 4
- (c) 5
- (d) 6

[Hint: The structure of Ni-DMG complex is,



- 4. Which of the following is not a chelate?
  - (a) Cis-platin—a drug used in the treatment of cancer
  - (b) Haemoglobin—a protein present in blood
  - (c) Chlorophyll—a green plant pigment which acts as a photosensitizer in the synthesis of carbohydrates
  - (d) Vitamin B<sub>12</sub>—it is a cobalt (I) complex which is essential for growth of animals
- 5. Which of the following statements are correct about stability of chelates?
  - (a) As the number of rings in complex increases, stability of chelate also increases
  - (b) A chelate having five membered ring is more stable if it contains double bonds
  - (c) A chelate having six membered ring is more stable if it does not contain double bonds
  - (d) Chelating ligands are atleast bidentate ligands
- 6. Chelate effect refers to:
  - (a) increase in reactivity of complex because of chelation
  - (b) increase in stability of complex due to chelation
  - (c) increase in conductivity of complex due to chelation
  - (d) decrease in stability of complex due to chelation

### **THOUGHT 2**

Coordination compounds play a vital role in our lives. The importance of these compounds can be realised from the fact that life would not have been possible without the existence of chlorophyll in plants and haemoglobin in the blood of the animals. The field of such compounds has expanded very fast in recent years and coordination compounds are playing important roles in analytical chemistry, polymerisation reactions, metallurgy and refining of metals, organic synthesis, electroplating, biochemistry, water purification, textile dyeing and bacteriology.

- 1. The hardness of water is estimated by:
  - (a) Conductivity method
- (b) EDTA method
- (c) Titrimetric method
- (d) Distillation-method
- 2. A reagent used for identifying nickel ion is:
  - (a) Potassium ferrocvanide (b) Phenolphthalein
  - (c) Dimethyl glyoxime
- (d) EDTA
- 3. Lead poisoning in the body can be removed by:
  - (a) Zeise's salt
- (b) Ferrocene
- (c) Cis-platin
- (d) [Ca(EDTA)]<sup>2</sup>
- 4. Extraction of Ag from sulphide ore and removal of unreacted silver halide from photographic plate involve complexes:
  - (a)  $[Ag(CN)_2]^T$ ,  $[Ag(S_2O_3)_2]^{3-}$
  - (b)  $[Ag(S_2O_3)_2]^{3-}$ ,  $[Ag(CN)_2]^{-}$
  - (c) [Ag(CN)<sub>2</sub>] in both
- (d)  $[Ag(S_2O_3)_2]^{3-}$  in both
- Which is used in cancer chemotherapy?
  - (a) Cis-platin
- (b) Zeise's salt
- (c) Ferrocene
- (d) Fischer's salt

### THOUGHT 3

When crystals of CuSO<sub>4</sub> 4NH<sub>3</sub> are dissolved in water, there is hardly any evidence for the presence of Cu<sup>2+</sup> ions or ammonia molecules. A new ion, [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, is furnished in which ammonia molecules are directly linked with the metal ion. Similarly, the aqueous solution of Fe(CN)2.4KCN does not give tests of Fe<sup>2+</sup> and CN ions but gives test of a new ion,  $[Fe(CN)_6]^4$ . The ions  $[Cu(NH_3)_4]^{2+}$  and  $[Fe(CN)_6]^{4-}$  are called complex ions. These ions are represented as:

$$\begin{bmatrix} NH_3 \\ \downarrow \\ H_3N \longrightarrow Cu \longleftarrow NH_3 \\ \uparrow \\ NH_3 \end{bmatrix}^{2+} ; \begin{bmatrix} NC & CN \\ NC \longrightarrow Fe \longleftarrow CN \\ NC & CN \end{bmatrix}^{4-}$$

- 1. The primary and secondary valency of copper in the complex Cu(NH<sub>3</sub>)<sub>4</sub>SO<sub>4</sub> are:
  - (a) 2, 4
- (b) 4, 2
- (c) 0, 4
- (d) 1, 4

2. The EAN of Fe in  $[Fe(CN)_6]^{4-}$  ion is :

(a) 24

(b) 30

(d) 38

3. The hybrid state of Cu in  $[Cu(NH_3)_4]^{2+}$  is:

(a)  $sp^3$ 

(b)  $sp^2d$ 

(c)  $sp^3d^2$ 

(d)  $dsp^2$ 

**4.**  $[Fe(CN)_6]^{4-}$  ion is:

- (a) square planar
- (b) octahedral
- (c) tetrahedral
- (d) none of these
- 5. Which one of the following statements is correct?
  - (a)  $[Cu(NH_3)_4]^{2+}$  is diamagnetic while  $[Fe(CN)_6]^{4-}$  is paramagnetic
  - (b)  $[Cu(NH_3)_4]^{2+}$  is paramagnetic while  $[Fe(CN)_6]^{4-}$  is diamagnetic
  - (c) Both are paramagnetic (d) Both are diamagnetic
- **6.** For a complex ion,  $[Cu(NH_3)_4]^{2+}$ :
  - (a) stability constant is  $[Cu(NH_3)_4]^{2+}/[Cu^{2+}][NH_3]^4$
  - (b) stability constant is  $[Cu^{2+}][(NH_3)_4]/[Cu(NH_3)_4]^{2+}$
  - (c) stability is more if instability constant is higher
  - (d) stability is less if stability constant is higher

# THOUGHT 4

The coordination number of Ni<sup>2+</sup> is 4.

 $NiCl_2 + KCN \longrightarrow A$  (Cyano complex)

 $NiCl_2 + Conc. HCl (excess) \longrightarrow B (Chloro complex)$ 

- 1. The IUPAC names of A and B are:
- [I.I.T. 2006]
- (a) Potassium tetracyanonickelate(II), potassium tetrachloridonickelate (II)

- (b) Tetracyanopotassiumnickelate (II), tetrachloridopotassiumnickelate(II)
- (c) Tetracyanonickel(II), tetrachloridonickel (II)
- (d) Potassium tetracyanonickel(II), potassium tetrachloridonickel(II)
- 2. Predict the magnetic nature of A and B:
  - (a) both are diamagnetic
  - (b) A is diamagnetic and B is paramagnetic with one unpaired
  - (c) A is diamagnetic and B is paramagnetic with two unpaired electrons
  - (d) both are paramagnetic
- 3. The hybridization of A and B are:

(a)  $dsp^2$ ,  $sp^3$ 

(c)  $dsp^2$ ,  $dsp^2$ 

(d)  $sp^3d^2$ ,  $d^2sp^3$ 

[Hint: Cyano complex K<sub>2</sub>[Ni(CN)<sub>4</sub>]

Potassium tetracyanonickelate (II)

Chloro complex K2[NiCl4]

Potassium tetrachloridonickelate(II)

3dCyano complex

> $dsp^2$ diamagnetic

Chloro complex

3d

sp<sup>3</sup> paramagnetic ]

\*\*\*

# tuswers

Thought 1 Thought 2

2. (d) 2. (c) 3. (c) 3. (d)

5. (a, d) 4. (a) **4.** (a)

**4.** (b)

5. (a) 5. (b)

6. (a)

6. (b)

Thought 3 1. (a) 2. (c) 3. (d) Thought 4 1. (a) 2. (c) 3. (a)

1. (d)

1. (b)

# BRAIN STORMING PROBLEMS

- 1. Write down the IUPAC names of the following complexes:
  - (i)  $(NH_4)_2[FeF_5H_2O]$
  - (ii)  $[Co(NH_3)_5H_2O](ReO_4)_3$
  - (iii)  $[Co(H_2O)(NH_3)_5][Co(C_2O_4)_3]$
  - (iv)  $[Co(H_2O)(NH_3)_5][Cr(SCN)_4(NH_3)_2]_3$
  - (v)  $[Co(H_2O)(NH_3)_5][Co(NO_2)_4(NH_3)_2]_3$
  - (vi)  $K_4[Mo(CN)_8]$
- (vii)  $(NH_4)_2[Cr(NH_3)(NCS)(S)]$
- (viii)  $[Bi \{SC(NH_2)_2\}_2](SO_4)$  (ix)  $[(CH_3)_4N]_2[Co(NCS)_4]$
- 2. [V(CO)<sub>6</sub>] has a magnetic moment corresponding to one unpaired electron. Draw a valence bond structure for this molecule. What is geometrical structure of complex?
- 3. Indicate whether of the following complexes are low spin or high spin complexes:

- [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>
- 0 unpaired electron
- $K_4[Cr(CN)_6]$ [Pt(NH3)6]Cl4
- 2 unpaired electrons 0 unpaired electron
- (NH<sub>4</sub>)<sub>2</sub>[FeF<sub>5</sub>H<sub>2</sub>O]
- 5 unpaired electrons
- 4. Arrange the following complexes in increasing order of molar conductivity (on the basis of Werner's theory):
  - (a)  $K[Co(NH_3)_3(NO_2)_4]$
  - (b)  $[Cr(NH_3)_3(NO_2)_3]$
  - (c)  $[Cr(NH_3)_5(NO_2)_3][Co(NO_2)_6]_2$
  - (d) Mg[Cr(NH<sub>3</sub>)(NO<sub>2</sub>)<sub>5</sub>]
  - [Ans. (b) < (a) < (d) < (c)]
- 5. Write down the formula corresponding to the following IUPAC names.
  - (i) Aluminium tetrachloridoaurate(III)

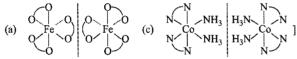
- (ii) Diamminesilver(I) hexacvanoferrate(II)
- (iii) Tetrahydroxodiaquoaluminate(III) ion
- (iv) Hexaamminecobalt(III) tetrachloridodiammine chromate(III)
- (v) Hexaamminenickel(II) hexanitrocobaltate(III)

[Ans. (i) Al[AuCl<sub>4</sub>]<sub>3</sub>

- (ii) [Ag(NH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>[Fe(CN)<sub>6</sub>]
- (iii)  $[Al(H_2O)_2(OH)_4]^-$  (iv)  $[Co(NH_3)_6][Cr(NH_3)_2Cl_4]_3$
- (v)  $[Ni(NH_3)_6]_3[Co(NO_2)_6]_2$
- **6.** How many geometrical isomers are possible for each of the following complexes? Draw the structure of each isomer:
  - (a)  $Pt(NH_3)_2(SCN)_2$
- (b) [CoCl<sub>2</sub>Br<sub>2</sub>]<sup>2-</sup>tetrahedral
- (c)  $Co(NH_3)_3(NO_2)_3$
- (d) Pt(en)Cl<sub>2</sub>
- (e)  $\left[\operatorname{Cr}(\operatorname{en})_2\operatorname{Br}_2\right]^+$
- $(f_{\bullet}) [Rh(en)_3]^{3+}$

[Ans. (a) Two (b) None (c) Two (d) None (e) Two (f) None]

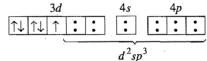
- 7. Which of the following complexes can exist as optical isomers (enantiomers)? Draw the structure of each enantiomer:
  - (a)  $[Fe(C_2O_4)_3]^{3-}$
- (b)  $[Co(NH_3)_4(en)]^{34}$
- (c)  $[Co(NH_3)_2(en)_2]^{3+}$
- (d)  $[Cr(H_2O)_4Cl_2]^{24}$



**8.**  $[Fe(CN)_6]^{3-}$  ion has magnetic moment of 1.41 B.M. while  $[Fe(H_2O)_6]^{3+}$  has a magnetic moment of 5.92 B.M. Explain.

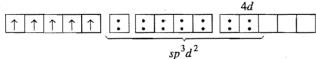
[Ans.  $[Fe(CN)_6]^3$  has one unpaired electron  $(d^2sp^3)$  hybridization of  $Fe^{3+}$ ) while  $[Fe(H_2O)_6]^{3+}$  has five unpaired electrons  $(sp^3d^2)$  hybridization of  $Fe^{3+}$ ,

[Fe(CN)<sub>6</sub>]<sup>3-</sup>



Mag. moment =  $\sqrt{2}$  = 1.414 B.M.

 $[Fe(H_2O)_6]^{3+}$ 



Mag. moment =  $\sqrt{5 \times 7} = \sqrt{35} = 5.92$  B.M.]

9. Match the geometry (given in column A) with the complex (given in column B).

(A)

(B)

- (i) Tetrahedral
- (a)  $[Cu(NH_3)_4]^2$
- (ii) Octahedral
- (b)  $[Ag(NH_3)_2]^{+}$
- (iii) Square planar
- (c) Fe(CO)<sub>5</sub>
- (iv) Trigonal bipyramidal
- (d)  $[Cr(H_2O)_6]^3$

- (v) Linear
- (e) [NiCL<sub>1</sub>]<sup>2</sup>-

[Ans. (i-e); (ii-d); (iii-a); (iv-c); (v-b)]

- 10. How many ions are given by the following complexes in aqueous solution?
  - (i) Ni(CO)<sub>4</sub>
- (ii) CoCl<sub>3</sub>·5H<sub>2</sub>O
- (iii) PtCl<sub>4</sub>·6NH<sub>3</sub>
- (iv) Cr(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>

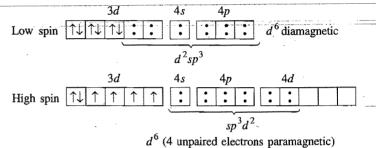
[Ans. (i) No ionisation

- (ii)  $[Co(H_2O)_5Cl] Cl_2 \rightleftharpoons [Co(H_2O)_5Cl]^{2+} + 2Cl^-$ ; three ions
- (iii)  $[Pt(NH_3)_6]Cl_4 \rightleftharpoons [Pt(NH_3)_6]^{4+} + 4Cl^-$ ; five ions
- (iv) [Cr(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>] no ionisation]
- 11. What d electron configurations exhibit both high and low spin in octahedral complexes?

[Ans.  $d^4$ ,  $d^5$ ,  $d^6$ ,  $d^7$ ]

- 12. Depict high spin and low spin configurations for each of the following complexes. Tell whether each is diamagnetic or paramagnetic. Give the number of unpaired electrons for the paramagnetic complexes:
  - (a)  $[Fe(CN)_6]^{4-}$
- b) [Co(NH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup>
- (c)  $[Fe(H_2O)_6]^{3+}$
- (d) [CrFa]<sup>4</sup>

[Ans. (a)  $[Fe(CN)_6]^{4-}$ :

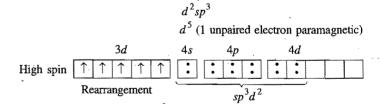


(b)  $\left[\text{Co(NH}_3)_6\right]^{3+}$ :  $d^6$  Case depiction as in (a)

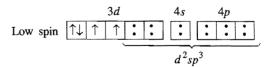
Low spin diamagnetic; high spin paramagnetic (4 unpaired electrons)

(c)  $[Fe(H_2O)_6]^{3+}$ :

Low spin

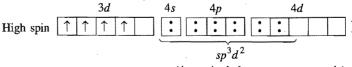


(d)  $[CrF_6]^{4-}$ :  $d^4$  Case



(2 unpaired electrons paramagnetic)

 $d^5$  (5 unpaired electrons paramagnetic)



(4 unpaired electrons paramagnetic)

13. Draw the structure of geometrical isomers of  $[Pt(gly)_2]$  where  $gly \rightarrow NH_2CH_2COO^-$ .

[Ans. 
$$CH_2 - NH_2$$
  $OC - O$   $OCO$ 

**14.** How many geometrical isomers with formula [MABCD] e.g., [Pt(NH<sub>3</sub>)(py)(NH<sub>2</sub>OH) NO<sub>2</sub>]<sup>+</sup> are possible?

[Ans. 3]

[Hint:



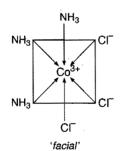
**15.**—Give the example of a tetrahedral complex showing optical activity.

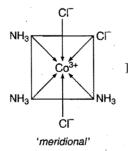
[Ans.

$$H_3C$$
 $C=0$ 
 $Be$ 
 $C=0$ 
 $CH$  and its mirror image
 $C_6H_5$ 
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**16.** What are *facial* and *meridional* isomers? Explain with examples.

[Ans. For the complexes of the type [Ma<sub>3</sub>b<sub>3</sub>] e.g., [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>] and [Rh(py)<sub>3</sub>Cl<sub>3</sub>]; the isomer is called facial (fac) when all similar ligands occupy same face of an octahedron as shown below. When all similar ligands are not on the same face then the isomer is called meridional (mer).





17. Explain why [Cu(en)<sub>2</sub>]<sup>2+</sup> is less stable than [Fe(EDTA)]<sup>-</sup>?

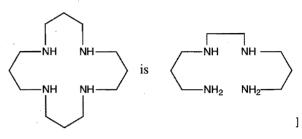
[Ans. [Cu(en)<sub>2</sub>]<sup>2+</sup> has four rings in the structure. On the other hand [Fe(EDTA)]<sup>-</sup> has five rings in the structure.

$$\begin{bmatrix} \mathsf{CH}_2 - \mathsf{NH}_2 & \mathsf{NH}_2 - \mathsf{CH}_2 \\ \mathsf{CH}_2 - \mathsf{NH}_2 & \mathsf{CU}^2 + \mathsf{NH}_2 - \mathsf{CH}_2 \\ \mathsf{CH}_2 - \mathsf{NH}_2 & \mathsf{CH}_2 \end{bmatrix}^{2+} \\ \begin{bmatrix} \mathsf{C} & \mathsf{C} & \mathsf{C} \\ \mathsf{C} & \mathsf{C} & \mathsf{C} \\ \mathsf{C} & \mathsf{C} & \mathsf{C} \\ \mathsf{C} & \mathsf{C} & \mathsf{C} \\ \mathsf{C} \\ \mathsf{C} & \mathsf{C} \\ \mathsf{C} & \mathsf{C} \\ \mathsf{C} \\ \mathsf{C} & \mathsf{C} \\ \mathsf{C} \\ \mathsf{C} & \mathsf{C} \\ \mathsf{C} \\ \mathsf{C} & \mathsf{C} \\ \mathsf{$$

Greater is the number of rings of chelation, more is the stability of complex. Thus, [Fe(EDTA)]<sup>-</sup> is more stable than [Cu(en)<sub>2</sub>]<sup>2+</sup>.]

18. What do you understand by macrocyclic effect?

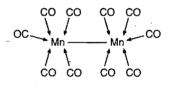
[Ans. Thermodynamic stability of a complex formed with a cyclic polydentate ligand is increased when compared to the complex formed with a non-cyclic ligand.



19. The EAN of each Mn(Z = 25) in  $Mn_2(CO)_{10}$  is 36. What is the structure of this complex?

[Ans. EAN = 25 (electrons from Mn atom) + 10 (electrons from five CO ligand) +1 (electron from Mn—Mn bond)

Thus, structure will be:



**20.** How many different structures are possible for each of the following complex ions?

(a)  $[Co(NH_3)_5H_2O]^{3+}$ 

(b)  $[Co(NH_3)_4(H_2O)_2]_0^{3+}$ 

(c)  $[Co(NH_3)_3(H_2O)_3]^{3+}$ 

(d)  $[Co(NH_3)_2(H_2O)_4]^{3+}$ 

[Ans. Draw the structures yourself.]

21. The hexaaqua complex,  $[Ni(H_2O)_6]^{2+}$ , is green, whereas the corresponding ammonia complex,  $[Ni(NH_3)_6]^{2+}$ , is violet. Explain.

[Ans. NH<sub>3</sub> is a stronger ligand than H<sub>2</sub>O, so [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> will absorb higher energy light than [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>. Being green, [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is probably absorbing red light while violet, [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> is probably absorbing higher energy yellow-green light.]

22. Which of the following metal ions cannot form both highspin and low-spin octahedral complexes?

(a)  $Ti^{3+}$ 

(b)  $Co_{2+}^{2+}$ 

(c)  $Fe^{2+}$ 

(d) Cu<sup>2+</sup>

[Ans. (a) and (d)]

23. Rank the following complex ions in order of increasing  $\Delta$ :  $[Cr(NH_3)_6]^{3+}, [Cr(H_2O)_6]^{3+}, [Cr(NO_2)_6]^{3-}.$ 

[Ans.  $[Cr(H_2O)_6]^{3+} < [Cr(NH_3)_6]^{3+} < [Cr(NO_2)_6]^{3-}$ .]

**24.** The value of  $\Delta$  for  $[RhCl_6]^{3-}$  is 243 kJ mol<sup>-1</sup>. What wavelength of light will promote an electron from the  $t_{2g}$  set to the  $e_g$  set? What is the colour of the complex?

[Hint:  $\Delta = hv = h$ .  $\frac{c}{\lambda}$  for one electron

or 
$$\lambda = \frac{h \cdot c}{\Delta} = \frac{6.63 \times 10^{-34} \text{Js} \times 3 \times 10^8 \text{ms}^{-1} \times 6.02 \times 10^{23}}{243 \times 10^3 \text{J}}$$
  
= 492 × 10<sup>-9</sup> m = 492 nm, orange]

### INTEGER ANSWER Type Questions

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. How many number of unpaired electrons are present in  $d^6$ , low spin octahedral complex?
- 2. On treatment of 100 mL of 0.1 *M* solution of the complex CoCl<sub>3</sub>·6NH<sub>3</sub> with excess of AgNO<sub>3</sub>, 4.305 g of AgCl was obtained. What is the positive charge present on the complex ion?
- 3. The possible number of geometrical isomers for the complex  $[Pt(NH_3)(NH_2OH)(NO_2)(py)]NO_2$  are:

- **4.** The oxidation number of M in the compound  $[M(NH_3)_5SO_4]$  is:
- 5. A certain complex ion has the formula  $[M(en)_2Br_2]^+$  where M is the metal ion and en = ethylene diamine. How many isomers are possible for this?
- 6. What is the value of spin only magnetic moment value of  $Cr(CO)_6$ ?
- 7. How many unpaired electrons are present in  $[Fe(H_2O)_5NO]SO_4$  complex?
- **8.** How many H-bonds are present in the complex entity formed for Ni<sup>2+</sup> and dimethylglyoxime?

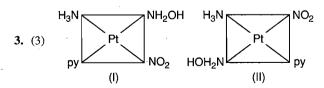
### Answers

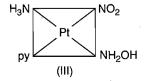
1. (0) Octahedral complex has  $d^2sp^3$  hybridisation.

2. (3) Number of moles of complex =  $\frac{0.1}{1000} \times 100 = 0.01$  mole

Number of moles of AgNO<sub>3</sub> =  $\frac{4.305}{143.5}$  = 0.03 mole

This shows that three chloride ions are present in the complex. The formula is  $[Co(NH_3)_6]Cl_3$ .





- 4. (2)
- 5. (3) Geometrical isomers, cis form has optical isomer.
- **6.** (0) In  $Cr(CO)_6$ , there is no unpaired electron.
- 7. (3) The oxidation state of Fe in the complex is +1. Thus Fe<sup>+</sup> has configuration  $3d^7$ . Thus, there are three unpaired electrons.

8. (2) 
$$CH_3 - C = N$$
  $N = C - CH_3$   $CH_3 - C = N$   $N = C - CH_3$   $N = C - CH_3$ 

- 53. What is the crystal field splitting energy or crystal field stabilisation energy (CFSE) for d' configuration for strong ligand field?
  - (a)  $-1.6 \Delta_0$
- (b)  $-2.0 \Delta_0$
- (c)  $-2.4 \Delta_0$
- (d)  $-1.8 \Delta_0$
- 54. In the following complexes of manganese what is the distribution of electrons on d-orbitals of manganese?
  - (i)  $[Mn(H_2O)_6]^{2+}$
- (ii) [Mn(CN)<sub>6</sub>]<sup>4</sup>
- (a)  $t_{2g}^3 e_g^2$  in both
- (b)  $t_{2g}^5 e_g^0$  in both
- (c)  $t_{2g}^3 e_g^2$  in (i) and  $t_{2g}^5 e_g^0$  in (ii)
- (d)  $t_{2g}^5 e_g^0$  in (i) and  $t_{2g}^3 e_g^2$  in (ii)

#### Passage 2

The d-block elements include the most common metal used in construction and manufacturing, metals that are valued for their beauty, metals used in coins and metals used in modern technology. The d-block elements include the densest elements, the metals with the highest melting and lowest melting points. Some of the members are radioactive and certain d-block elements are particularly important in living organisms. A number of compounds of d-block elements are used for special purposes.

- 55. Which of the element possesses the highest melting point?
  - (a) La

(b) W

(c) S

- (d) Pt
- **56.** Which of the element possesses highest density?

(b) Ag

(c) Au

- (d) Ir
- **57.** How many d-block elements are radioactive in nature?

(b) 9

(c) 10

- (d) 11
- 58. Wilkinson's catalyst is a transition metal complex in which the metal is:
  - (a) Rh

(b) Ru

(c) Fe

(d) Ni

### iswers with Hints

1. (a) The magnetic moment depends on the number of unpaired electrons.

> Mag. moment =  $\sqrt{n(n+2)}$  where n is the number of unpaired electrons.

 $Ti^{3+}$ 

→ Minimum mag. moment

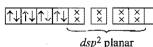
Ni<sup>2+</sup>  $3d^7$ 

Co<sup>2+</sup>

 $Mn^{2+}$ 

- 2. (b)
- 3.
  - (d) (c)  $[Fe(CN)_6]^{4-}$  $Fe^{2+}3d^{6}$  $d^2sp^3$  octahedral diamagnetic

 $[Ni(CN)_4]^{2+}$  $Ni^{2+}3d^{8}$ 



Ni(CO)<sub>4</sub>

diamagnetic

 $Ni^{6}3d^{10}$ sp3 tetrahedral diamagnetic

- (a) Cu<sup>+</sup> is colourless as it contains completely filled d-orbitals.
- (c)  $2CrO_A^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$
- 7. (b)  $Cu^{2+} + 2CN^{-} \longrightarrow Cu(CN)_2 \longrightarrow Cu_2(CN)_2$  $Cu_2(CN)_2 + 6KCN \longrightarrow 2K_3[Cu(CN)_4]$ i.e.,  $[Cu(CN)_4]^{3-}$  is formed in which Cu(I) is present which is colourless.
- 8. (c) Only primary valencies are ionised.

$$\begin{split} [\text{Co(NH}_3)_5\text{Cl}]\text{Cl}_2 & \longleftarrow \underbrace{[\text{Co(NH}_3)_5\text{Cl}]^{2^+} + 2\text{Cl}^-}_{3 \text{ ions}} \\ & \xrightarrow{-2\text{AgNO}_3} 2\text{AgCl} + [\text{Co(NH}_3)_5\text{Cl}](\text{NO}_3)_2 \end{split}$$

(a) The oxides with lower oxidation states are basic while with higher oxidation states are acidic.

> The oxides with intermediate states are amphoteric. CrO and V2O3 are basic in nature. Mn2O7 is an acidic oxide. Cr<sub>2</sub>O<sub>3</sub> shows amphoteric nature.

**10.** (b) Cis-[Co(en)(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> exists in optically active forms.

$$\begin{bmatrix} Cl \\ Cl \\ NH_3 \end{bmatrix}^+ \begin{bmatrix} Cl \\ Cl \\ H_3N \end{bmatrix}$$

$$NH_3$$

11. (a) Magnetic moment depends on the number of unpaired electrons.

$$Cr^{3+}$$
  $\uparrow \uparrow \uparrow \uparrow \uparrow \stackrel{\times}{\searrow} \stackrel{\times}{\times}$ 

One unpaired electron

 $\times$   $\times$   $\times$   $\times$  No unpaired electron ↑↓ × ×

 $3d^{10} sp^3d^2$ 

No unpaired electron

12. (c) Higher the oxidation state of the metal greater is the crystal field splitting. The species (c) is in the +3 oxidation state while others are in +2 state.

- 34. (A) KCN gives K<sub>3</sub>[Cu(CN)<sub>4</sub>] complex compound with CuSO<sub>4</sub>
  - (R) KCN reduces Cu<sup>2+</sup> to Cu<sup>+</sup> and then forms a complex
- 35. (A) Silver is recovered from argentocyanide complex by adding zinc dust.
  - (R) Zinc is less electropositive than silver.
- 36. (A) Scandium and zinc are two members of first transition series which do not form coloured compounds.
  - (R) Scandium compounds have  $3d^0$  configuration while zinc compounds have  $3d^{10}$  configuration, i.e., there is no d-d
- 37. (A) The highest oxidation state of manganese is +6.
  - (R) The highest oxide formed by manganese is acidic in
- 38. (A)  $[Fe(CN)_6]^{3-}$  is weakly paramagnetic while  $[Fe(CN)_6]^{4-}$  is diamagnetic.
  - (R) Both  $[Fe(CN)_6]^3$  and  $[Fe(CN)_6]^4$  involve  $d^2sp^3$ hybridisation. In rearranging electrons in d-orbitals, one d-orbital is singly occupied in [Fe(CN)<sub>6</sub>]<sup>3-</sup> and all d-orbitals are doubly occupied in  $[Fe(CN)_6]^4$ .
- 39. (A) The order of increasing crystal field splitting in the three complexes of iron is:

 $[FeCl_6]^{4-} < [Fe(H_2O)_6]^{2+} < [Fe(H_2O)_6]^{3+}$ 

- (R) The crystal field splitting depends on the position of ligand in the spectrochemical series and oxidation state of central metal ion.
- **40.** (A)  $[Cr(H_2O)_2(C_2O_4)_2]^-$  shows geometrical isomerism.
  - (R) [Co(NH<sub>3</sub>)<sub>5</sub>(NO<sub>2</sub>)] (NO<sub>3</sub>)<sub>2</sub> shows ionisation and linkage isomerism.

#### MATRIX MATCHING QUESTIONS

41. Match Column-II with Column-II:

#### Column-I

#### Column-II

- (a) Mercury
- (m) d-block element
- (b) Lanthanum
- (n) f-block element
- (c) Uranium
- (o) Radioactive element
- (d) Technetium
- (e) Americium
- (p) Synthetic element
- (q) Variable valency
- 42. Match Column-II with Column-II:

#### Column-I

#### Column-II

- (a)  $K_2MnO_4$
- (p) Transition element in +6 oxidation state
- (b) KMnO<sub>4</sub>
- (q) Oxidising agent in acid medium
- (c) K<sub>2</sub>CrO<sub>4</sub>
- (r) Obtained from pyrolusite ore
- (d)  $K_2Cr_2O_7$
- (s) Obtained from chromite ore
- 43. Match Column-I with Column-II:

#### Column-I

#### Column-II

- (a)  $[Fe(CN)_6]^4$
- (q) Diamagnetic
- (b)  $[Cu(NH_3)_4]^{2+}$ (c)  $[Mn(CN)_6]^2$
- (r) Unpaired electron or electrons

(p) Paramagnetic

- (d)  $[CuCl_4]^{2-}$
- (s)  $sp^3$ -hybridisation
- (e)  $[Fe(CN)_6]^{3}$
- (t)  $d^2sp^3$ -hybridisation
- 44. Match Column-I with Column-II:

#### Column-I

#### Column-II

- (a) [Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl
- (p) Linkage isomerism
- (b) [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]
- (q) Optical isomerism
- (c) [Cr(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>]Cl<sub>2</sub>
- (r) Geometrical isomerism
- (d)  $[Co(en)_3]Cl_3$
- (s) Ionisation isomerism

#### INTEGER ANSWER TYPE

- 45. The effective atomic number (EAN) of a metal carbonyl,  $M(CO)_x$  is 36. The atomic number of M is 26. The value of x
- 46. A weak field complex of Ni<sup>2+</sup> has magnetic moment value of 2.82 BM. The number of electrons in the  $t_{2g}$  level of Ni<sup>2+</sup> will
- 47. The number of unpaired electrons present in chromium atom
- 48. The number of NaCl molecules in the following balanced equation is:

$$K_2Cr_2O_7 + H_2SO_4 + NaCl \longrightarrow KHSO_4 + NaHSO_4 + CrO_2Cl_2 + H_2O$$

- 49. In hydrated ferric chloride, how many water molecules are coordinated to iron ion?
- 50. What is the oxidation state of the central metal atom in [Fe(EDTA)] complex ion?

#### LINKED COMPREHENSION TYPE

#### Passage 1

In octahedral complexes with six ligands surrounding the metal atom/ion, the degeneracy of d-orbitals is disturbed due to repulsions between the ligands and d-orbitals. The repulsions between  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals and the ligands are greater than  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals and ligands. Thus, there is splitting of d-orbitals into two sets, i.e., two orbitals of higher energy,  $e_e$  set and three orbitals of lower energy,  $t_{2g}$  set. The difference of energy between the two sets of d-orbitals is called crystal field splitting energy and is represented by  $\Delta_0$ . For any given metal cation, the magnitude of  $\Delta_0$  depends upon the nature of the ligands. Some ligands produce strong fields and hence splitting is large whereas some others produce weak fields and hence they result in small splitting of *d*-orbitals.

- **51.** In an octahedral crystal field,  $e_g$ , orbitals are:
  - (a) raised in energy by  $0.4 \Delta_0$
  - (b) lowered in energy by  $0.6 \Delta_0$
  - (c) raised in energy by  $0.6 \Delta_0$
  - (d) lowered in energy by  $0.4 \Delta_0$
- **52.** Predict the order of  $\Delta_0$  for the following complexes:
  - (A)  $[Fe(H_2O)_6]^{2+}$ , (B)  $[Fe(CN)_4(H_2O)_2]^{2-}$ , (C)  $[Fe(CN)_6]^4$
  - (a) (A) < (B) < (C)
- (b) (B) < (C) < (A)
- (c) (C) < (B) < (A)
- (d) (B) < (A) < (C)

	(c) $[PtCl(dien)]Cl, [NiCl_2Br_2]^2$		(c) La is an element of transition series rather than lanthanoid
	(d) $[Co(NO_3)_3(NH_3)_3]$ , $Cis$ - $[Pt(en)_2Cl_2]$		series.
20.	For which of the following species d-d transition does not		(d) Atomic radius of Zr and Hf is same due to lanthanoid
	account for its colour?	27	contraction.
	(a) $Cr_2O_7^{2-}$	27.	Which of the following is not correct for $[Cr(NH_3)_6]Cl_3$ ?  (a) It gives white precipitate with AgNO <sub>3</sub> .
	(c) $CrO_2Cl_2$ $\Box$ (d) All of these $\Box$	•	(a) It gives white precipitate with AgNO <sub>3</sub> .
21.	Mn <sup>2+</sup> forms a complex with Br <sup>-</sup> ion. The magnetic moment		(c) It is dramagnetic.
	of the complex is 5.92 BM. The probable formula and		(d) It is colourless.
	geometry of the complex is:	28.	Identify the false statements.
	(a) $[MnBr_4]^{2-}$ ; tetrahedral		(a) The hybridisation of Cr in $[Cr(H_2O)_6]Cl_3$ is $d^2sp^3$ .
	(b) $[MnBr_4]^{2-}$ ; square planar		(b) Both $K_2[PtCl_6]$ and $K_2[NiCl_6]$ are stable coordination
	(c) $[MnBr_6]^{4-}$ ; octahedral		compounds.
	(d) $[MnBr_5]^{3-}$ ; trigonal bipyramid		(c) The paramagnetic character in 3d transition series ions
22.	Which one of the following statements is not correct?		$(M^{2+})$ increases upto manganese and then decreases. $\square$
	(a) Argentite is impure AgCl.		(d) Zn is not considered a transition metal.
	(b) Ag and Au are extracted by making soluble cyanide	29.	Identify the incorrect statements.
	complexes.		(a) Chlorophyll is a Co(II) Complex. □
	(c) German silver does not contain silver.		(b) Chlorophyll is a $Mg(II)$ Complex.
00	(d) Zinc is used to extract silver from lead-silver alloy.		(c) Chlorophyll is an organometallic compound.
23.			(d) Chlorophyll is a diamagnetic compound.
٠	(a) different shapes of f-orbitals $\Box$	30.	Identify the incorrect statements.
	(b) efficient shielding by $f$ -orbitals for the attraction of $ns^2$ electrons by the nucleus		(a) $\Delta_{tetrahedral}$ is 4/9 th $\Delta_{octahedral}$ .
	(c) efficient shielding by $d$ and $f$ -orbitals for the attraction		(b) Number of unpaired electrons in $K_3[CoF_6]$ are zero. $\square$
	of $ns^2$ electrons by the nucleus		(c) The hybridisation of Cr in $[Cr(H_2O)_6]SO_4$ is $d^2sp^3$ . $\square$
•	(d) inefficient shielding by f-orbitals for the attraction of $ns^2$		(d) In a tetrahedral complex $d_{xy}$ , $d_{xz}$ , $d_{yz}$ orbitals set has higher energy than the $d_{xy}$ , $d_{xy}$ orbitals set.
	electrons by the nucleus	31.	- $        -$
24.	Which of the following statements is correct regarding the	51.	(a) $[NiCl_4]^{2-}$ $\Box$ (b) $[CuCl_4]^{2-}$ $\Box$
	slag obtained during the extraction of a metal like copper or		(c) $[MnCl_4]^{2-}$ $\Box$ (d) $[Ni(CN)_4]^{2-}$ $\Box$
	iron?	32	Select the correct statements.
	(a) The slag is lighter and has lower melting point than the	32.	(a) Complex ions in which ligands can be interchanged
	metal.		rapidly are said to be non-labile.
	(b) The slag is heavier and has lower melting point than the		(b) Chelation effect is maximum for five or six membered
	metal.		rings.
	(c) The slag is lighter and has higher melting point than the		(c) $[Fe(CN)_6]^4$ and $[Fe(H_2O)_6]^{2+}$ can be distinguished by
	metal.		magnetic moment.
	(d) The slag is heavier and has higher melting point than		(d) For a given ion and ligand, greater the charge on the
25	the metal. $\Box$ In the extraction of copper, the reaction which does not take		metal ion, greater is the stability. $\Box$
Δ٥.	place in Bessemer converter is:		
	(a) $2\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2$	AS	SSERTION-REASON TYPE QUESTIONS
	(a) $2\operatorname{Cu}_2\operatorname{O} + \operatorname{Cu}_2\operatorname{S} \longrightarrow 6\operatorname{Cu} + \operatorname{SO}_2$ $\square$	J	Each of the following questions contains Assertion (A) and
	(c) $2Cu_2O + Cu_2O + 2SO_2$ $\square$	Rea	ason (R). Use the following key to select one appropriate answer.
	(d) $2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2$		(a) If (A) and (R) both are true and (R) is a correct explanation for (A).
OV	IE OR MORE THAN ONE CORRECT		(b) If (A) and (R) both are true and (R) is not a correct
	ISWERS TYPE		explanation for (A).
			(c) If (A) is true and (R) is false.
26.	Identify the correct statements.		(d) If (A) is false and (R) is true.
	(a) La(OH) <sub>3</sub> is less basic than Lu(OH) <sub>3</sub> . $\Box$	33.	(A) K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> has orange colour due to charge transfer.
	(b) In lanthanoid series, the ionic radius of Ln <sup>3+</sup> ions		(R) In dichromate, two tetrahedral sharing one oxygen atom
	decreases.		at one corner are present.

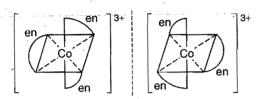
# Revision Exercise (Chapter 14 to 15)

IN	GLE CORRECT ANSWER TYPE			(c) $[Co(NH_3)_6]^{3+}$	]
1.	The ion of least magnetic moment among the following i	s :		(d) $[Fe(CN)_6]^{3-}$	]
			11.	Which one of the following complex ions has the highest	t
	(a) $Ti^{3+}$			magnetic moment?	
2.	Cu <sup>2+</sup> is more stable than Cu <sup>+</sup> due to reduction potent	tial		(a) $[Cr(NH_3)_6]^{3+}$	]
	which is due to hydration energy.			(c) $[Fe(CN)_6]^{4+}$ $\Box$ (d) $[Zn(NH_3)_6]^{2+}$ $\Box$	]
	(a) lower, lower   (b) lower, higher		12	The crystal field stabilization energy (CFSE) is the highest	t
	(c) higher, higher   (d) higher, lower		1 2,4,	for:	٠
3.	In the series Sc $(Z = 21)$ to Zn $(Z = 30)$ , the enthalpy	of		(a) $[CoF_4]^{2-}$	1
	atomisation is lowest for which element?		•	(c) $[Co(NH_3)_6]^{3+}$	
	(a) Sc		. 12.	Which of the following reaction is not taking place during	
		0	15.	the extraction of Ag from $Ag_2S$ by cyanide process?	5
4.	Out of $[Fe(CN)_6]^{4-}$ , $[Ni(CN)_4]^{2-}$ and $Ni(CO)_4$ :				-
	(a) all have identical shapes			(a) $Ag_2S + 4CN^- \longrightarrow 2[Ag(CN)_2]^- + S^{2-}$	
	(b) all are paramagnetic			(b) $\operatorname{Zn} + 2[\operatorname{Ag}(\operatorname{CN})_2]^{-} \longrightarrow [\operatorname{Zn}(\operatorname{CN})_4]^{2^{-}} + 2\operatorname{Ag}\downarrow \qquad \Box$	
	(c) all are diamagnetic			(c) $\operatorname{Cu} + 2[\operatorname{Ag}(\operatorname{CN})_2]^- \longrightarrow [\operatorname{Cu}(\operatorname{CN})_4]^2 + 2\operatorname{Ag}\downarrow \square$	]
	(d) $[Fe(CN)_6]^{4-}$ is diamagnetic but $[Ni(CN)_4]^{2-}$ and $Ni(CC)_{4-}$			(d) $S^{2-}$ $\longrightarrow$ $SO_4^{2-} + S + S_2O_3^{2-}$	_
_	are paramagnetic		14.	When a Ti3+ complex is irradiated by light of certain	n
J.	Which one of the following ions is colourless?			wavelength, the complex appears coloured. The electronic	c
	(a) $Cu^+$			transition which is responsible for the colour is:	
_	(c) $Ni^{2+}$ $\square$ (d) $Fe^{3+}$ The yellow colour of chromates changes to orange			(a) $t_{2g}^0 e_g^1 \longrightarrow t_{2g}^1 e_g^0$ $\square$ (b) $t_{2g}^1 e_g^1 \longrightarrow t_{2g}^0 e_g^2$ $\square$	]
U.	acidification due to the formation of :	OII		(c) $t_{2g}^1 e_g^0 \longrightarrow t_{2g}^0 e_g^1  \Box$ (d) $t_{2g}^2 e_g^0 \longrightarrow t_{2g}^1 e_g^1  \Box$	]
	(a) $Cr^{3+}$ $\Box$ (b) $Cr_2O_3$		15	Mark the correct statement.	_
	(a) $Cr_2O_7^2$		10.	(a) $[Co(C_2O_4)_3]^{3-}$ is paramagnetic, inner orbital complex. $\square$	7
~	<u> </u>			(b) $[Co(C_2O_4)_3]^{3-}$ is diamagnetic, outer orbital complex. $\Box$	
1.	Cu <sup>2+</sup> is a blue coloured solution. The blue colour vanishing KCN as help in addition. Which are the followers.				
	when KCN solution is added. Which of the follow	ıng		(c) $[Co(C_2O_4)_3]^{3-}$ is paramagnetic, outer orbital complex.	
	compounds is formed?	_		(d) $[Co(C_2O_4)_3]^{3-}$ is diamagnetic, inner orbital complex.	
		. 🗆	16.	An excess of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> reacts with aqueous CuSO <sub>4</sub> to give	:
	(c) $Cu(OH)_2$ $\Box$ (d) $CuCN$			(a) $CuS_2O_3$ $\square$ (b) $Cu_2S_2O_3$	J
8.	One mole of Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sub>3</sub> gives three moles of ions			(c) $Na_2[Cu(S_2O_3)_2]$	J
	dissociation in water. One mole of this reacts with two mo	oles	17.	In which of the following cases, the stability of two oxidation	n
	of AgNO <sub>3</sub> to give two moles of AgCl. The complex is:		1	states is correctly represented?	
	(a) $[Co(NH_3)_4Cl_2]Cl \cdot NH_3$			(a) $Ti^{3+} > Ti^{4+}$	J
	(b) $[Co(NH_3)_4Cl]Cl_2 \cdot NH_3$			(c) $Fe^{2+} > Fe^{3+}$	J
	(c) $[Co(NH_3)_5Cl]Cl_2$		18.	Carbon and CO gas are used to reduce which of the following	g
	(d) $[Co(NH3)3Cl3] \cdot 2NH3$			pairs of metal oxides for extraction of metals?	0
9.	The amphoteric oxide among the following is:			(a) FeO, SnO $\square$ (b) SnO, ZnO $\square$	J
	(a) $Cr_2O_3$ $\Box$ (b) $Mn_2O_7$			(c) BaO, $Na_2O_2$ $\square$ (d) FeO, ZnO	J
	(c) $V_2O_3$ $\square$ (d) CrO		19.	In which of the following pairs both the complexes show	N
10.	The optically active coordination complex ion among	the		optical isomerism?	
	following is:			(a) $Cis$ -[Cr(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> Cl <sub>2</sub> ], $Cis$ -[Cr(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]	J
	(a) $Trans$ - $[Co(en)_2Cl_2]^+$			(b) [Co(en) <sub>3</sub> ]Cl <sub>3</sub> , Cis-[Co(en) <sub>2</sub> Cl <sub>2</sub> ]Cl	J
	(b) $Cis$ -[Co(en)(NH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup>				

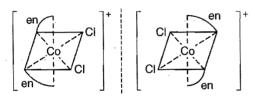
- 13. (c)
- 14. (c) 15. (d)  $Co^{3+}$  configuration  $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow$  $d^2sp^3$  hybridisation

Hence, the complex is diamagnetic and inner orbital.

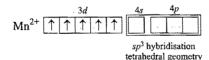
- **16.** (d)  $CuSO_4 + Na_2S_2O_3 \longrightarrow CuS_2O_3 + Na_2SO_4$  $2CuS_2O_3 + Na_2S_2O_3 \longrightarrow Cu_2S_2O_3 + Na_2S_4O_6$  $3Cu_2S_2O_3 + 2Na_2S_2O_3 \longrightarrow Na_4[Cu_6(S_2O_3)_5]$
- 17. (b)  $Mn^{2+}(3d^5)$  is more stable than  $Mn^{3+}(3d^4)$ .
- $FeO + C \longrightarrow Fe + CO$ 18. (d)  $FeO + CO \longrightarrow Fe + CO_2$  $ZnO + C \longrightarrow Zn + CO$  $ZnO + CO \longrightarrow Zn + CO_2$
- 19. (b) [Co(en)3]Cl3



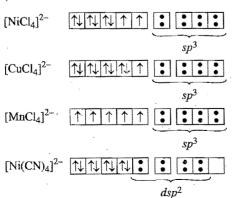
Cis-[Co(en)2Cl2]Cl



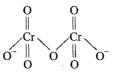
- **20.** (d)
- 21. (a) Magnetic moment = 5.92 BM Number of unpaired electrons = 5



- 22. (a) Argentite is Ag<sub>2</sub>S or silver glance.
- (d) 24. (a) 25. (a) 26. (b, c, d) 27. (b, d) 28. (a, b)
- **29.** (a, c) **30.** (b, c)
- 31. (a, b, c)



- 32. (b, c, d) Complex ion in which ligands can be interchanged rapidly are said to be labile.
- 33. (b) Both (A) and (R) are true.



#### Structure of dichromate ion

- (a) Both (A) and (R) are true and (R) is correct explanation of (A).
- (c) Zinc is more electropositive than silver. Thus, (A) is correct while (R) is wrong.
- (a) Both (A) and (R) are true and (R) is correct explanation of (A).
- (d) (A) is not correct. The highest oxidation state of manganese is +7. (R) is correct.
- 38. (a) Both (A) and (R) are true and (R) is correct explanation of (A).
- (a-m); (b-m); (c-n, o, q); (d-m, o, p, q); (e-n, o, p, q).
- (a-p, r); (b-q, r); (c-p, s); (d-p, q, s) 42.
- (a-q, t); (b-p, r); (c-p, r, t); (d-p, r, s); (e-p, r, t).
- (a-q, r); (b-r); (c-p, s); (d-q).
- 45. (5)

$$EAN = 36 = 26 + 2 \times x$$

or 
$$2x = 10$$

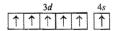
or 
$$x = 5$$

**46.** (6) 
$$\mu = 2.82 = \sqrt{n(n+2)}$$

i.e., 
$$n=2$$

2 unpaired electrons are present, i.e., Ni<sup>2+</sup> configuration is 3d<sup>8</sup>. The number of electrons on  $t_{2g}$  are six.

47.



48.  $K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl \longrightarrow 2KHSO_4 + 4NaHSO_4$ 

$$+ 2 \text{CrO}_2 \text{Cl}_2 + 3 \text{H}_2 \text{O}_3$$

(6) [Fe(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>

50. (3) 
$$x + 1 \times (-4) = -1$$
  
or  $x = +3$ 

- (c) In octahedral complex,  $e_g$  orbitals are raise in energy by 0.6  $\Delta_0$ .
- **52.** (a) The value of  $\Delta_0$  depends on the nature of the ligand. H<sub>2</sub>O is a weak field ligand while CN is a strong field ligand. The  $\Delta_0$ increases as the number of CN ligands increases.
- **53.** (d)  $d^7 = t_{2g}^6 e_g^1$  (for strong ligand field)  $= [6 \times (-0.4) + 0.6] \Delta_0$  $= -1.8 \Delta_0$
- 54. (c) H<sub>2</sub>O is weak field ligand while CN is a strong field ligand. In (i) complex, the distribution is  $t_{2g}^3 e_g^2$ , i.e., all the electrons are unpaired while in (ii) complex, the distribution is  $t_{2g}^3 e_g^0$ , i.e., two  $t_{2g}$  orbitals are paired while one is unpaired.
- (b) **56.** (d)
- (d) Technetium and 10 members of 4th d-block series are radioactive in nature.
- 58. (a)

# CHAPTER 16

# Stoichiometry

(Calculations Based on Chemical Equations)

#### Contents:

- 16.1 Introduction
- 16.2 Calculations Involving Mass-Mass Relationship
- 16.3 Calculations Involving Mass-Volume Relationship
- 16.4 Calculations Involving Volume-Volume Relationship

#### 16.1 INTRODUCTION

A chemical equation\* is a short-hand method of depicting a chemical change with the help of chemical symbols and formulae and it relates both the qualitative and quantitative aspects of a chemical change. As a symbol or a formula has a quantitative meaning, in the same fashion, an equation formed with them also gives quantitative information relating the ingredients (reacting materials) and the products of the reaction.

Calculations based on chemical equations are known as **stoichiometric** calculations. Calculations based on chemical equations are of three types:

- (i) Calculations involving mass-mass relationship.
- (ii) Calculations involving mass-volume relationship.
- (iii) Calculations involving volume-volume relationship.

# 16.2 CALCULATIONS INVOLVING MASS-MASS RELATIONSHIP

In general, the following steps are adopted in making necessary calculations:

- (i) Write down balanced molecular equation of the chemical change.
- (ii) Write down the number of moles below the formula of each of the reactants and products.
- (iii) Write down the relative masses of the reactants and products with the help of formula below the respective formula. These shall be theoretical amounts of reactants and products.
- (iv) By the application of unitary method or the rule of three, the unknown factor is determined.

<sup>\*</sup>For details, consult Chapter 1, Physical Chemistry for Competitions.

**Problem 1.** How many grams of oxygen are required to burn completely 570 g of octane?

#### **Solution:**

Balanced equation of the chemical change is:

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$
2 mole 25 mole 2 × 114 25 × 32

For burning  $2 \times 114$  g of octane, oxygen required

$$= 25 \times 32 \text{ g}$$

For burning 1 g of octane, oxygen required

$$=\frac{25\times32}{2\times114}\,\mathrm{g}$$

Thus, for burning 570 g of octane, oxygen required

$$=\frac{25\times32}{2\times114}\times570$$

**Problem 2.** Calculate the number of grams of magnesium chloride that could be obtained from 17.0 g of HCl when HCl is reacted with excess of magnesium oxide.

#### **Solution:**

Balanced equation of the chemical change is:

MgO + 2HCl 
$$\longrightarrow$$
 MgCl<sub>2</sub> + H<sub>2</sub>O  
1 mole 2 mole 1 mole 1 mole 2 × 36.5 g (24 + 71) g 95 g  
73 g of HCl produce MgCl<sub>2</sub> = 95 g  
1 g of HCl produce MgCl<sub>2</sub> =  $\frac{95}{73}$  g 95

17 g of HCl will produce 
$$MgCl_2 = \frac{95}{73} \times 17$$
 g = 22.12 g

**Problem 3.** The amount of carbon monoxide in a gas sample can be determined by using the reaction,

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

If a gas sample liberates 0.384 g of  $I_2$ , how many grams of CO were present in the sample?

#### Solution:

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$
 $\begin{array}{ccc}
5 & \text{mole} & & 1 & \text{mole} \\
5 \times 28.0 & & & 253.8 & g
\end{array}$ 

253.8 g of iodine liberated when CO is present in the sample =  $5 \times 28$  g

1 g of iodine liberated when CO is present in the sample

$$=\frac{5\times28}{253.8}$$
 §

0.384 g of iodine liberated when CO is present in the sample

$$= \frac{5 \times 28}{253.8} \times 0.384 = 0.212 \text{ g}$$

**Problem 4.** Calculate the weight of iron which will be converted into its oxide by the action of 18 g of steam.

[M.L.N.R. 1996]

#### **Solution:**

The balanced equation for the chemical change is:

$$3Fe + 4H2O \longrightarrow Fe3O4 + 4H2$$
3 mole 4 mole
3 × 56 g 4 × 18 g
$$4 \times 18 \text{ g of steam convert iron into } Fe3O4 = 3 \times 56 \text{ g}$$

1 g of steam converts iron into 
$$Fe_3O_4 = \frac{3 \times 56}{4 \times 18}$$
 g

18 g of steam convert iron into 
$$Fe_3O_4 = \frac{3 \times 56}{4 \times 18} \times 18$$
 g = 42 g

**Problem 5.** Calculate the residue obtained on strongly heating 2.76 g  $Ag_2CO_3$ .

#### **Solution:**

The balanced equation for the chemical change is:

$$Ag_2CO_3 \xrightarrow{\text{Heat}} 2Ag + CO_2 + \frac{1}{2}O_2$$
1 mole 2 mole
276 g 2 × 108 g

f Ag\_2CO\_2 give silver on heating = 2

276 g of 
$$Ag_2CO_3$$
 give silver on heating = 216 g

2.76 g of Ag<sub>2</sub>CO<sub>3</sub> give silver on heating = 
$$\frac{216}{276} \times 2.76$$
 g = 2.16 g

#### Limiting Reagent

In general, when a chemical reaction is carried out, one of the reagents will be used in excess of the amount required. The reagent that is not present in excess is the one that will determine how much product can be obtained and is thus referred to as the limiting reagent. The reagent that gives the least number of moles of the product is the limiting reagent.

With the help of limiting reagent, the amount of the excess reagent which has been utilised and the amount remaining can be calculated. This can be clearly understood from the following problems:

**Problem 6.** 100 g sample of calcium carbonate is reacted with 70 g of orthophosphoric acid. Calculate:

- (a) the number of grams of calcium phosphate that could be produced.
- (b) the number of grams of excess reagent that will remain unreacted.

#### **Solution:**

The balanced equation is:

100 g of CaCO<sub>3</sub> would produce 
$$Ca_3(PO_4)_2 = \frac{310}{300} \times 100$$
  
= 103 g  
= 0.33 mole

196 g of 
$$H_3PO_4$$
 produce  $Ca_3(PO_4)_2 = 310$  g or 1 mole  
70 g of  $H_3PO_4$  would produce  $Ca_3(PO_4)_2 = \frac{310}{196} \times 70$   
= 110.7 g  
= 0.356 mole

The above values tell that CaCO<sub>3</sub> is the limiting reagent. Hence, calcium phosphate formed is 0.33 mole or 103 g. For producing 103 g of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub> required will be

$$=\frac{196}{310} \times 103 = 65.12 \text{ g}$$

Mass of remaining orthophosphoric acid = (70 - 65.12)= 4.88 g

**Problem 7.** What is the maximum mass of  $Al(OH)_3$  that can be prepared by reaction of 13.4 grams of  $AlCl_3$  with 10 grams of NaOH according to the following equation?

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$$

#### Solution:

The balanced equation is:

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$$
1 mole 3 mole 1 mole
133.5 g 120 g 78.0 g

133.5 g of AlCl<sub>3</sub> produce Al(OH)<sub>3</sub> = 78.0 g

13.4 g of AlCl<sub>3</sub> produce Al(OH)<sub>3</sub> = 
$$\frac{78.0}{133.5}$$
 × 13.4 = 7.829 g

120 g of NaOH produce  $Al(OH)_3 = 78 g$ 

10 g of NaOH produce Al(OH)<sub>3</sub> = 
$$\frac{78}{120}$$
 × 10 = 6.5 g

Hence, NaOH is a limiting reagent. Thus,  $Al(OH)_3$  produced in the reaction is 6.5 g.

**Problem 8.** 200 grams of marble chips are dropped into 100 g of hydrochloric acid. How much chips will remain undissolved? What weight of anhydrous calcium chloride and what weight of carbon dioxide gas could be obtained from it?

#### **Solution:**

The balanced equation for the chemical change is:

Since marble chips remain undissolved, HCl is a limiting reagent.

73 g of HCl react with 
$$CaCO_3 = 100 \text{ g}$$

100 g of HCl will react with 
$$CaCO_3 = \frac{100}{73} \times 100$$

Weight of chips undissolved = 200-136.986= 63.014g

73 g of HCl produce  $CaCl_2 = 111$  g

100 g of HCl will produce 
$$CaCl_2 = \frac{111}{73} \times 100 = 152.05 \text{ g}$$

73 g of HCl produce 
$$CO_2 = 44$$
 g

100 g of HCl will produce 
$$CO_2 = \frac{44}{73} \times 100 = 60.27$$
 g

#### Calculations Involving Per cent Yield

In general, when a reaction is carried out in the laboratory we do not obtain actually the theoretical yield of the product. The amount of the product that is actually obtained is called the actual yield. Knowing the actual yield and theoretical yield, the per cent yield can be calculated by the following formula:

Per cent yield = 
$$\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

**Problem 9.** A 7.8 g sample of  $C_6H_6$  reacts with excess of  $HNO_3$  to produce 9.0 g of  $C_6H_5NO_2$ . What is the per cent yield of  $C_6H_5NO_2$  in this experiment?

#### Solution:

The balanced equation is:

$$\begin{array}{cccc} C_6H_6 \ + \ HNO_3 \longrightarrow & C_6H_5NO_2 \ + \ H_2O \\ \hline 1 \ mole & 1 \ mole & 1 \ mole \\ \hline 78 \ g & 123 \ g \end{array}$$

78 g of benzene produce  $C_6H_5NO_2 = 123 \text{ g}$ 

7.8 g of benzene will produce 
$$C_6H_5NO_2 = \frac{123}{78} \times 7.8$$
  
= 12.3 g

i.e., theoretical yield of 
$$C_6H_5NO_2 = 12.3 g$$

Actual yield = 
$$9.0 g$$

Per cent yield = 
$$\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$
  
=  $\frac{9.0}{12.3} \times 100 = 73.17$ 

**Problem 10.** If  $4.80 \text{ g of } N_2F_4$  is obtained when 4.00 g of  $NH_3$  is reacted with  $14.0 \text{ g of } F_2$  according to the following reaction,

$$2NH_3 + 5F_2 \longrightarrow N_2F_4 + 6HF$$

what is the per cent yield?

#### **Solution:**

The balanced equation is:

34 g of NH<sub>3</sub> react with fluorine = 190 g

4 g of NH<sub>3</sub> react with fluorine = 
$$\frac{190}{34} \times 4$$
  
= 22.35 g

This shows that fluorine is a limiting reagent.

190.0 g of fluorine produce 
$$N_2F_4 = 104.0$$
 g

14.0 g of fluorine produce 
$$N_2F_4 = \frac{104.0}{190.0} \times 14.0$$
  
= 7.66 g

*i.e.*, theoretical yield = 
$$7.66 \text{ g}$$

Actual yield = 4.80 g  
Per cent Yield = 
$$\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$
  
=  $\frac{4.80}{7.66} \times 100 = 62.66$ 

#### Successive Reactions

In such reactions, the products of one reaction are used up in one or more subsequent reactions. For solving these problems, balanced and molecular equations are written for all reactions involved separately. The individual equations are multiplied as a whole by suitable factors in order to cancel out the products of one reaction which are utilized in the subsequent reactions. The unknown factors are now equated with the known factors and their values are thus determined.

**Problem 11.** Find out the weight of calcium carbonate that must be decomposed to produce sufficient quantity of carbon dioxide to convert 10.6 g of sodium carbonate completely into sodium bicarbonate.

#### Solution:

The balanced equations are:

1 mole 1 mole 100 g 44 g

106 g Na<sub>2</sub>CO<sub>3</sub> are completely converted into NaHCO<sub>3</sub> by 44 g of CO<sub>2</sub>.

10.6 g Na<sub>2</sub>CO<sub>3</sub> are completely converted into NaHCO<sub>3</sub> by CO<sub>2</sub>

$$=\frac{44}{106}\times10.6=4.4$$
 g

From equation (ii), it is clear that,

44 g of  $CO_2$  is obtained from  $CaCO_3 = 100$  g

4.4 g of CO<sub>2</sub> is obtained from 
$$CaCO_3 = \frac{100}{44} \times 4.4 = 10$$
 g

Problem 12. From the following reaction sequence,

$$Cl_2 + 2KOH \longrightarrow KCl + KClO + H_2O$$
  
 $3KClO \longrightarrow 2KCl + KClO_3$   
 $4KClO_3 \longrightarrow KCl + 3KClO_4$ 

calculate the mass of chlorine needed to produce 50 g of  $KClO_4$ .

#### **Solution:**

The given balanced equations are:

$$[Cl_2 + 2KOH \longrightarrow KCl + KClO + H_2O] \times 12$$

$$[3KClO \longrightarrow 2KCl + KClO_3] \times 4$$

$$4KClO_3 \longrightarrow KCl + 3KClO_4$$

Adding 
$$12\text{Cl}_2 + 24\text{KOH} \longrightarrow 21\text{KCl} + 3\text{KClO}_4 + 12\text{H}_2\text{O}$$
  
 $12 \text{ mole}$  3 mole  
 $12 \times 71 \text{ g}$  3 × 138.5 g

 $3 \times 138.5$  g of KClO<sub>4</sub> are obtained by the use of chlorine =  $12 \times 71$  g

50 g of KClO<sub>4</sub> will be obtained by the use of chlorine

$$= \frac{12 \times 71}{3 \times 138.5} \times 50$$
$$= 102.527 \text{ g}$$

**Problem 13.** 1 gram of pyrolusite was boiled with excess of concentrated HCl and the issuing gas was passed through a solution of potassium iodide when 1.27 g of iodine were liberated. What was the percentage of pure  $MnO_2$  in the pyrolusite sample? [Mn = 55; Cl = 35.5; K = 39; I = 127]

#### **Solution:**

The following equations are involved in the problem:

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

Adding 
$$MnO_2 + 4HCl + 2KI \rightarrow MnCl_2 + 2KCl + 2H_2O + I_2$$
  
1 mole 1 mole  $87 \text{ g}$   $2 \times 127 \text{ g}$ 

 $2 \times 127$  g of  $I_2$  are obtained from manganese dioxide

1.27 g of I<sub>2</sub> are obtained from manganese dioxide

$$= \frac{87}{2 \times 127} \times 1.27 = 0.435 \text{ g}$$

Percentage of purity of pyrolusite  $=\frac{0.435}{1} \times 100 = 43.5$ 

#### Composition of Mixtures

**Problem 14.** 2.662 grams of a mixture of potassium chloride and sodium chloride gave on treatment with silver nitrate solution, 5.752 grams of dry silver chloride. Find the percentage composition of the mixture.

$$[Na = 23; K = 39.1; Cl = 35.5; Ag = 108]$$

#### **Solution:**

Let x g NaCl be present in the mixture.

The amount of KCl in the mixture = (2.662 - x) g

The reactions which occur in the formation of AgCl are:

(i) NaCl + AgNO<sub>3</sub> 
$$\longrightarrow$$
 AgCl + NaNO<sub>3</sub>

1 mole
1 mole
143.5 g

(ii) 
$$KCl + AgNO_3 \longrightarrow AgCl + KNO_3$$
1 mole 1 mole
74.6 g 143.5 g

$$58.5 \text{ g NaCl give AgCl} = 143.5 \text{ g}$$

x g NaCl give AgCl = 
$$\frac{143.5 \times x}{58.5}$$
 = 2.453x g

$$74.6 \text{ g KCl give AgCl} = 143.5 \text{ g}$$

$$(2.662 - x)$$
 g KCl give AgCl =  $\frac{143.5 \times (2.662 - x)}{74.6}$   
=  $(5.12 - 1.924 \ x)$  g

So, 
$$2.453x + (5.12 - 1.924x) = 5.752$$

or 
$$0.529x = 0.632$$
  
 $x = \frac{0.632}{0.529} = 1.195 \text{ g}$ 

The mixture contains NaCl = 1.195 g

Percentage of NaCl = 
$$\frac{1.195}{2.662} \times 100 = 44.89$$

Percentage of KCl = (100 - 44.89) = 55.11

**Problem 15.** Determine the percentage composition of a mixture of anhydrous sodium carbonate and sodium bicarbonate from the following data:

Mass of the mixture taken = 3.0 g

Loss in mass on heating = 0.186 g

$$[Na = 23; C= 12; O= 16]$$

#### **Solution:**

On heating only sodium bicarbonate will decompose according to the following equation:

Loss = (168 - 106) g = 62 g

62 g loss occur when sodium bicarbonate heated = 168 g 0.186 g loss occur when sodium bicarbonate heated

$$=\frac{168}{62}\times0.186=0.504$$

Percentage of NaHCO<sub>3</sub> = 
$$\frac{0.504}{3.0} \times 100 = 16.8$$

Percentage of anhydrous  $Na_2CO_3 = (100 - 16.8)$ 

= 83.2

**Problem 16.** A mixture of FeO and Fe<sub>3</sub>O<sub>4</sub> when heated in air to constant weight gains 5% in its weight. Find the composition of initial mixture. [Fe = 55.8; O = 16]

#### Solution:

Let the total mass of mixture be = 100 g

Let the mass of FeO be x g and that of Fe<sub>3</sub>O<sub>4</sub> will be (100 - x) g. Both the oxides on heating are converted into Fe<sub>2</sub>O<sub>3</sub> according to following equations:

(i) 
$$2\text{FeO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{Fe}_2\text{O}_3$$
  
143.6 g 159.6 g

(ii) 
$$2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \longrightarrow 3\text{Fe}_2\text{O}_3$$
  
 $462.8 \text{ g}$   $478.8 \text{ g}$ 

Mass of Fe<sub>2</sub>O<sub>3</sub> produced from x g of FeO =  $\frac{159.6 \times x}{143.6}$  g

Mass of  $Fe_2O_3$  produced from (100 - x) g of  $Fe_3O_4$ 

$$=\frac{478.8}{462.8}\times(100-x)$$
 g

Total mass of  $Fe_2O_3$  produced = 105 g

So, 
$$\frac{159.6 \times x}{143.6} + \frac{478.8}{462.8} (100 - x) = 105$$

On solving

x = 20.78

Hence, the initial composition of the mixture is:

FeO = 20.78% and  $Fe_3O_4 = 79.22\%$ 

# 16.3 CALCULATIONS INVOLVING MASS-VOLUME RELATIONSHIP

These calculations are based on the fact that 1 mole or 1 g molecule of the substance occupies 22.4 litres or 22400 mL at N.T.P. The following example shows the mass-volume relationship:

Volume of a gas at any temperature and pressure can be converted into mass or *vice-versa* with the help of equation,

$$PV = \frac{w}{M}RT$$

where w is the mass of the gas, M is the molecular mass and R is molar gas constant.

**Problem 17.** Calculate the volume of carbon dioxide at N.T.P. evolved by strong heating of 20 g calcium carbonate.

#### **Solution:**

The balanced equation is:

**Problem 18.** Calculate the volume of hydrogen liberated at 27°C and 760 mm pressure by treating 1.2 g of magnesium with excess of hydrochloric acid.

Solution: The balanced equation is:

$$\begin{array}{ccc} Mg + 2HCl & \longrightarrow MgCl_2 + H_2 \\ \text{l mole} & \text{l mole} \\ 24 \text{ g} & \text{22.4 litre} \\ & \text{at N.T.P.} \end{array}$$

24 g of Mg liberate hydrogen = 22.4 litre

1.2 g Mg will liberate hydrogen = 
$$\frac{22.4}{24} \times 1.2$$
  
= 1.12 litre

Volume of hydrogen under given condition can be calculated by applying,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$P_1 = 760 \text{ mm}$$

$$T_1 = 273 \text{ K}$$

$$V_1 = 1.12 \text{ litre}$$

$$V_2 = \frac{760 \times 1.12}{273} \times \frac{300}{760} = 1.2308 \text{ litre}$$

**Problem 19.** What quantity of copper (II) oxide will react with 2.80 litre of hydrogen at N.T.P.?

#### **Solution:**

The balanced equation is:

$$\begin{array}{ccc} CuO & + & H_2 \longrightarrow Cu + H_2O \\ 1 & mole & 1 & mole \\ 79.5 & g & 22.4 & litre \\ & at & N.T.P. \end{array}$$

22.4 litre of hydrogen at N.T.P. reduce CuO = 79.5 g

2.80 litre of hydrogen at N.T.P. will reduce CuO

$$=\frac{79.5}{22.4} \times 2.80 \text{ g} = 9.94 \text{ g}$$

**Problem 20.** 10 grams of a sample of potassium chlorate gave, on complete decomposition, 2.24 litre of oxygen at N.T.P. What is the percentage purity of the sample of potassium chlorate?

#### Solution:

The balanced equation of the decomposition is:

 $3 \times 22.4$  litre of oxygen obtained from KClO<sub>3</sub> = 245 g

2.24 litre of oxygen obtained from KClO<sub>3</sub> = 
$$\frac{245}{3 \times 22.4} \times 2.24$$
  
= 8.17 g

10 g of sample contains pure  $KClO_3 = 8.17$  g

Percentage purity of the sample = 
$$\frac{8.17}{10} \times 100 = 81.7$$

**Problem 21.** What volume of hydrogen at N.T.P. would be liberated by the action of zinc on 50 mL dilute  $H_2SO_4$  of 40% purity and having specific gravity of 1.3. [Zn = 63.5]

#### Solution:

Mass of 50 mL dilute  $H_2SO_4$  = volume × specific gravity

$$= 50 \times 1.3 = 65 \text{ g}$$

100 g of dilute  $H_2SO_4$  contain = 40 g  $H_2SO_4$ 

65 g of dilute 
$$H_2SO_4$$
 contain  $=\frac{40}{100} \times 65 = 26$  g

The reaction involved is:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
1 mole
1 mole
98 g
22.4 litre
at N.T.P.

At N.T.P. 98 g  $H_2SO_4$  liberate hydrogen with zinc = 22.4 litre

At N.T.P. 26 g H<sub>2</sub>SO<sub>4</sub> will liberate hydrogen with zinc

$$=\frac{22.4}{98} \times 26$$
 litre = 5.94 litre

**Problem 22.** At flash bulb used for taking photograph in poor light contains 30 mL of oxygen at a pressure of 780 mm at 27°C. Supposing that the initial wire flashed is pure magnesium which is oxidised to magnesium oxide in the process of flashing, calculate the minimum mass of magnesium wire that is to be needed for maximum efficiency.

#### **Solution:**

If V is the volume of oxygen at N.T.P., then

$$\frac{760 \times V}{273} = \frac{780 \times 30}{300}$$
$$V = 28 \text{ mL}$$

Mass of 22400 mL of oxygen at N.T.P. = 32 g 32 32 32

Mass of 28 mL of oxygen at N.T.P. = 
$$\frac{32}{22400} \times 28 = 0.04$$
 g

The reaction involved is:

$$\begin{array}{cccc}
2\text{Mg} & + & \text{O}_2 & \longrightarrow 2\text{MgO} \\
2 \times 2^4 & \text{g} & & 32 & \text{g}
\end{array}$$

32 g oxygen oxidise magnesium =  $2 \times 24$  g

0.04 g oxygen oxidise magnesium =  $\frac{2 \times 24}{32} \times 0.04 = 0.06$  g

# 16.4 CALCULATIONS INVOLVING VOLUME-VOLUME RELATIONSHIP

These calculations are based on two laws:

(i) Avogadro's law and (ii) Gay-Lussac's law. For example,

$$2NO$$
 +  $O_2$  =  $2NO_2$  (Avogadro's law)  
 $2 \text{ mole}$  1 mole 2 mole  
 $2 \times 22.4 \text{ litre}$  22.4 litre 2 × 22.4 litre

(Under similar conditions of temperature and pressure, equal moles of gases occupy equal volumes.)

or 
$$2NO + O_2 = 2NO_2$$
 (Gay-Lussac's law)  
2 vol 2 vol

(Under similar conditions, gases react in simple ratio of their volumes.)

**Problem 23.** What volume of oxygen gas at N.T.P. is necessary for complete combustion of 20 litre of propane measured at 27°C and 760 mm pressure?

#### **Solution:**

The balanced equation is:

$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$$
1 vol 5 vol
1 litre 5 litre

1 litre of propane required = 5 litre of oxygen

20 litre of propane will require =  $5 \times 20$ 

= 100 litre of oxygen at 760 mm and 27°C.

This volume will be converted to N.T.P. conditions. Given conditions,

$$P_1 = 760 \text{ mm}$$
  $P_2 = 760 \text{ mm}$   
 $T_1 = (27 + 273)\text{K} = 300 \text{ K}$   $T_2 = 273 \text{ K}$   
 $V_1 = 100 \text{ litre}$   $V_2 = ?$   
 $V_2 = \frac{760 \times 100}{300} \times \frac{273}{760} \text{ litre}$   
 $V_3 = 91.0 \text{ litre}$ 

**Problem 24.** One litre of a mixture of carbon monoxide and carbon dioxide is passed through a tube containing red hot charcoal. The volume now becomes 1.6 litre. Volumes are measured under similar conditions. Find the composition of gaseous mixture.

#### **Solution:**

When the mixture is passed over red hot charcoal, carbon dioxide present in the mixture is reduced to carbon monoxide. Thus, increase in volume is due to formation of CO from CO<sub>2</sub>.

The desired equation is: 
$$CO_2 + C = 2CO$$

Let x litre of  $CO_2$  be present in the mixture, the volume of carbon monoxide in the mixture = (1 - x) lit. x volume of CO<sub>2</sub> produce 2x volume of CO.

Total volume of CO = 
$$2x + 1 - x = 1 + x$$
  
= 1.6 litre (given)

So.

x = 0.6 litre

Volume of  $CO_2$  in the mixture = 0.6 litre

Volume of CO in the mixture = (1 - 0.6) = 0.4 litre

Problem 25. 1 litre of oxygen at N.T.P. is allowed to react with three times of carbon monoxide at N.T.P. Calculate the volume of each gas found after the reaction.

**Solution:** The desired equation is:

$$\begin{array}{cccc}
2CO & + & O_2 = 2CO_2 \\
2 & \text{vol} & 1 & \text{vol} & 2 & \text{vol}
\end{array}$$

1 vol of O2 reacts with 2 vol of CO

1 litre of O<sub>2</sub> reacts with 2 litre of CO

Thus,

1 litre of CO remains unreacted.

1 vol of  $O_2$  produces  $CO_2 = 2$  vol

or

1 litre of  $O_2$  will produce  $CO_2 = 2$  litre

Thus, gaseous mixture after the reaction consists,

Volume of 
$$CO = 1$$
 litre

Volume of  $CO_2 = 2$  litre

**Problem 26.** The percentage by volume of  $C_3H_8$  in a mixture of C<sub>3</sub>H<sub>8</sub>, CH<sub>4</sub> and CO is 36.5. Calculate the volume of CO<sub>2</sub> produced when 100 mL of the mixture is burnt in excess of  $O_2$ .

#### **Solution:**

The desired balanced equations are:

$$C_{3}H_{8} + 5O_{2} \longrightarrow 3CO_{2} + 4H_{2}O$$

$$1 \text{ vol} \qquad \qquad 3 \text{ vol}$$

$$CH_{4} + 2O_{2} \longrightarrow CO_{2} + 2H_{2}O$$

$$1 \text{ vol} \qquad \qquad 1 \text{ vol}$$

$$CO + \frac{1}{2}O_{2} \longrightarrow CO_{2}$$

$$1 \text{ vol} \qquad \qquad 1 \text{ vol}$$

Let a mL of C<sub>3</sub>H<sub>8</sub>, b mL of CH<sub>4</sub> and c mL of CO be present in 100 mL of mixture, then

$$a+b+c=100$$

Given

$$a = 36.5 \text{ mL}$$

So, 
$$b + c = (100 - 36.5) = 63.5 \text{ mL}$$

Volume of CO<sub>2</sub> formed = 
$$(3a + b + c)$$
  
=  $(3 \times 36.5 + 63.5)$  mL  
=  $109.5 + 63.5 = 173.0$  mL

Problem 27. The weight of one litre of ozonised oxygen at N.T.P. was found to be 1.5 g. When 100 mL of this mixture at N.T.P. were treated with turpentine oil, the volume was reduced to 90 mL. Hence, calculate the molecular mass of [M.L.N.R. 1996] ozone.

#### **Solution:**

Ozone is absorbed by turpentine oil.100 mL of ozonised

mixture is reduced to 90 mL with turpentine oil, i.e., 10 mL of ozone is present in 100 mL of the mixture.

1 L of mixture consists ozone = 100 mL

1 L of mixture consists oxygen = 900 mL

Let the molecular mass of ozone be M.

Mass of 100 mL of ozone = 
$$\frac{M}{22400} \times 100 = \frac{M}{224} g$$

Mass of 900 mL of oxygen = 
$$\frac{32}{22400} \times 900 = \frac{9}{7}$$
 g

So, 
$$\frac{M}{224} + \frac{9}{7} = 1.5$$

or 
$$M + 288 = 336$$

or 
$$M = 336 - 288 = 48$$

**Problem 28.** A gas mixture of 3 litre of propane  $(C_3H_8)$ and butane  $(C_4H_{10})$  on complete combustion at 25°C produced 10 litre  $CO_2$ . Find out the composition of gas mixture.

[M.L.N.R. 1992]

#### **Solution:**

Let a litre of C<sub>3</sub>H<sub>8</sub> and b litre of C<sub>4</sub>H<sub>10</sub> be present in mixture.

$$a + b = 3 \qquad \dots (i)$$

$$C_{3}H_{8} + 5O_{2} \longrightarrow 3CO_{2} + 4H_{2}O$$

$$1 \text{ vol} \qquad 3 \text{ vol}$$

$$C_{4}H_{10} + \frac{13}{2}O_{2} \longrightarrow 4CO_{2} + 5H_{2}O$$

$$1 \text{ vol} \qquad 4 \text{ vol}$$

$$^{4}$$
 vol  $^{2}$  CO<sub>2</sub> formed by  $^{2}$   $^{4}$   $^{2}$   $^{4}$   $^{2}$   $^{2}$   $^{4}$   $^{2}$   $^$ 

CO<sub>2</sub> formed by 
$$C_4H_{10} = 4b$$
  
  $3a + 4b = 10$  ... (ii)

Solving equations (i) and (ii),

$$a = 2$$
 litre

$$b = 1$$
 litre

### Some Miscellaneous Worked Problems

**Problem 29.** An impure sample of calcium carbonate contains 80% pure calcium carbonate. 25 g of the impure sample reacted with excess of hydrochloric acid. Calculate the volume of carbon dioxide at N.T.P. obtained from this sample.

#### Solution:

100 g of impure calcium carbonate contains

= 80 g pure calcium carbonate

25 g of impure calcium carbonate sample contains

$$=\frac{80}{100}\times25$$

= 20 g pure calcium carbonate

The desired equation is:

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$
1 mole
100 g
22.4 litre
at N.T.P.

100 g pure CaCO<sub>3</sub> liberate = 22.4 litre CO<sub>2</sub>

20 g pure 
$$CaCO_3$$
 liberate =  $\frac{22.4}{100} \times 20$   
= 4.48 litre  $CO_2$ 

**Problem 30.** A sample of hydrochloric acid contains 20% hydrochloric acid by weight. How much of this acid in grams is required for complete reaction with 50 g of calcium carbonate?

#### Solution:

The desired balanced equation is:

CaCO<sub>3</sub> + 2HCl = CaCl<sub>2</sub> + H<sub>2</sub>O + CO<sub>2</sub>  
<sup>1</sup> mole 2 mole  
<sup>100</sup> g 73 g  
100 g of CaCO<sub>3</sub> require = 73 g HCl  
50 g of CaCO<sub>3</sub> will require = 
$$\frac{73}{100} \times 50$$
  
= 36.5 g HCl

20 g of HCl is present in = 100 g sample 36.5 g of HCl is present in =  $\frac{100}{20} \times 36.5$  g sample = 182.5 g sample

Thus, 182.5 g of HCl sample is required for complete reaction with 50 g of calcium carbonate.

**Problem 31.** A mixture of aluminium and zinc weighing 1.67 g was completely dissolved in acid. 1.69 litre of hydrogen measured at 0°C and 1 atm. pressure was evolved. What was the weight of aluminium in the mixture?

**Solution:** Let the mixture contain aluminium x g.

The mixture contains zinc = (1.67 - x) g

Suppose the mixture is dissolved in H<sub>2</sub>SO<sub>4</sub>.

$$2A1 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2 \uparrow$$
  
2 × 27 g 3 × 22.4 litre  
at N.T.P.

 $2 \times 27$  g Al will evolve hydrogen =  $3 \times 22.4$  litre

$$x$$
 g Al will evolve hydrogen =  $\frac{3 \times 22.4}{2 \times 27}x$  litre  
Zn + H<sub>2</sub>SO<sub>4</sub>  $\longrightarrow$  ZnSO<sub>4</sub> + H<sub>2</sub>

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
65 g
22.4 litre
at N.T.P.

65 g of zinc evolve hydrogen = 22.4 litre

So, (1.67 - x) g of zinc will evolve hydrogen

$$=\frac{22.4}{65}(1.67-x)$$
 litre

Thus, 
$$\frac{3 \times 22.4}{2 \times 27} x + \frac{22.4}{65} (1.67 - x) = 1.69$$
or 
$$\frac{67.2}{54} x - \frac{22.4}{65} x = 1.69 - \frac{22.4 \times 1.67}{65}$$

$$x = 1.24$$

Weight of Al in the given mixture = 1.24 g

**Problem 32.** A 1.00 g sample of KClO<sub>3</sub> was heated under such conditions that a part of its decomposed according to the equation

$$(i) 2KClO_3 \longrightarrow 2KCl + 3O_2$$

and the remaining underwent change according to the equation,

(ii) 
$$4KClO_3 \longrightarrow 3KClO_4 + KCl$$

If the amount of oxygen evolved was 146.8 mL at S.T.P., calculate the percentage by weight of KClO<sub>4</sub> in the residue.

#### **Solution:**

67.2 litre of oxygen is evolved from = 245 g KClO<sub>3</sub> 0.1468 litre of oxygen will be evolved from

$$=\frac{245}{67.2}\times0.1468=0.5352$$
 g KClO<sub>3</sub>

Hence, KClO<sub>3</sub> left for (ii) reaction.

$$(1.00 - 0.5352) = 0.4648 \text{ g}$$
  
 $245 \text{ g KClO}_3 \text{ yield KCl} = 149 \text{ g}$   
 $0.5352 \text{ g KClO}_3 \text{ will yield KCl} = \frac{149}{245} \times 0.5352 \text{ g}$   
 $= 0.3254 \text{ g}$ 

Considering equation (ii),

0.4648 g KClO<sub>3</sub> will yield 
$$=\frac{415.5}{490} \times 0.4648$$
  
= 0.3941 g KClO<sub>4</sub>  
490g KClO<sub>3</sub> yield = 74.5 g KCl

$$0.4648 \text{ g KClO}_3 \text{ will yield} = \frac{74.5}{490} \times 0.4648$$
  
= 0.0707 g KCl

Total weight of residue = 
$$0.3254 + 0.3941 + 0.0707$$
  
=  $0.7902$  g  
% KClO<sub>4</sub> =  $\frac{0.3941}{0.7902} \times 100 = 49.8$ 

**Problem 33.** 1 g Mg is burnt in a closed vessel which contains 0.5 g of  $O_2$ .

- (i) Which reactant is left in excess?
- (ii) Find the weight of the excess reactant.

#### Solution:

The desired chemical equation is:

$$2Mg + O_2 \longrightarrow 2MgO$$
48 g of Mg react with oxygen = 32 g

1 g of Mg would react with oxygen = 
$$\frac{32}{48}$$
 = 0.67 g

However, only 0.5 g of O<sub>2</sub> is present. Hence, whole of Mg is not burnt and a part of left unreacted.

32 g of oxygen react with magnesium = 48 g  
0.5 g of oxygen would react with magnesium = 
$$\frac{48}{32}$$
 = 0.5 g  
= 0.75 g

Mass of magnesium left unreacted = (1.0 - 0.75) g = 0.25 g

**Problem 34.** 5 g of K<sub>2</sub>SO<sub>4</sub> were dissolved in 250 mL of solution. How many mL of this solution should be used so that 1.2 g of BaSO<sub>4</sub> may be precipitated from BaCl<sub>2</sub> solution? Solution:

The desired equation is:

233 g of BaSO<sub>4</sub> is obtained from = 174 g of K<sub>2</sub>SO<sub>4</sub>

1.2 g of BaSO<sub>4</sub> will be obtained from = 
$$\frac{174}{233} \times 1.2$$
  
= 0.8961 g of K<sub>2</sub>SO<sub>4</sub>

5 g of K<sub>2</sub>SO<sub>4</sub> is present in 250 mL of solution.

So, 0.8961 g of 
$$K_2SO_4$$
 will be present in  $\frac{250}{5} \times 0.8961$   
= 44.8 mL of solution

**Problem 35.** A 5.0 g mixture of lead nitrate and sodium nitrate was heated below  $600^{\circ}$ C until the mass of the residue was constant. If the loss of mass is 28%, find the mass of each component in the original mixture. [Pb = 207; N = 14; O = 16; Na = 23] [1.1.T. 1990]

#### **Solution:**

Let the mass of  $Pb(NO_3)_2$  in the mixture be x g. The mass of sodium nitrate = (50 - x) g The desired reactions in the problem are :

$$\begin{array}{c} \text{2Pb(NO}_3)_2 \longrightarrow \text{2PbO} + 4\text{NO}_2 + \text{O}_2 \\ \text{662 g} & \text{446 g} \\ \text{2NaNO}_3 \longrightarrow \text{2NaNO}_2 + \text{O}_2 \\ \text{170g} & \text{138g} \end{array}$$

Loss in mass is 28% of 5 g =  $\frac{28}{100} \times 5 = 1.4$  g

Mass of residue left = (5 - 1.4) = 3.6 g ... (i)

662 g lead nitrate produce on heating PbO = 446 g

x g lead nitrate would produce on heating PbO =  $\frac{446}{662} \times x$  g Similarly, 170 g NaNO<sub>3</sub> produce NaNO<sub>2</sub> on heating = 138 g

(5.0 - x) g NaNO<sub>3</sub> produce NaNO<sub>2</sub> on heating =  $\frac{138}{178} \times (5 - x)$ Total residue after heating

/ AAC 120

$$= \frac{446}{662}x + \frac{138}{170} \times (5 - x) \qquad \dots \text{ (ii)}$$

Equating (i) with (ii),

$$\frac{446}{662}x + \frac{138}{170}(5 - x) = 3.6$$

On solving,

$$x = 3.32$$

Mass of lead nitrate in mixture = 
$$3.32 \text{ g}$$
  
Mass of sodium nitrate in mixture =  $(5 - 3.32) \text{ g}$   
=  $1.68 \text{ g}$ 

**Problem 36.** A mixture of formic acid and oxalic acid is heated with conc.  $H_2SO_4$ . The gas produced is collected and on its treatment with KOH solution the volume of the gas decreases by one sixth. Calculate the molar ratio of the two acids in the original mixture. [Roorkee 1990]

#### **Solution:**

The reactions of the acids may be represented by the following equations:

Let the total volume of the gas collected be V litre. On passing through KOH solution,  $CO_2$  is absorbed and the volume of the gas decreases by one sixth.

Volume of CO<sub>2</sub> in the mixture = 
$$\frac{V}{6}$$
  
Volume of total CO =  $V - \frac{V}{6} = \frac{5V}{6}$ 

Volume of CO produced from  $H_2C_2O_4 = V/6$ 

Volume of CO produced from HCOOH 
$$=\frac{5V}{6} - \frac{V}{6} = \frac{4V}{6}$$

Moles of CO produced from HCOOH = 
$$\frac{4V}{6} \times \frac{1}{22.4}$$

Moles of CO produced from 
$$H_2C_2O_4 = \frac{V}{6} \times \frac{1}{22.4}$$

Thus,

$$\frac{\text{Moles of HCOOH}}{\text{Moles of H}_2\text{C}_2\text{O}_4} = \frac{\text{Moles of CO produced from HCOOH}}{\text{Moles of CO produced from H}_2\text{C}_2\text{O}_4}$$

$$=\frac{\frac{4V}{6} \times \frac{1}{22.4}}{\frac{V}{6} \times \frac{1}{22.4}} = \frac{4}{1}$$

The formic acid and oxalic acid in the original mixture are in the molar ratio of 4:1.

**Problem 37.** Chlorine gas can be produced in the laboratory by the reaction,

 $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$  if a 61.3 g sample that is 96%  $K_2Cr_2O_7$  is allowed to react with 320 mL of hydrochloric acid solution having a density 1.15 g mL<sup>-1</sup> and containing 30% HCl by mass, what mass of  $Cl_2$  is generated?

#### **Solution:**

The desired equation is:

$$\begin{array}{c} K_{2}Cr_{2}O_{7} + 14HC1 \longrightarrow 2KC1 + 2CrCl_{3} + 7H_{2}O + 3Cl_{2} \\ 294 \text{ g} & 14 \times 36.5 \text{ g} & 3 \times 71 \text{ g} \\ \\ \text{Mass of } K_{2}Cr_{2}O_{7} = \frac{96}{100} \times 61.3 = 58.848 \text{ g} \\ \end{array}$$

Mass of HCl= 
$$\frac{30}{100} \times 320 \times 1.15 = 110.4 \text{ g}$$
  
294 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> react with HCl = 511.0 g  
58.848 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> would react with HCl= $\frac{511.0}{294.0} \times 58.848 \text{ g}$   
= 102.28 g

Thus, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is a limiting reagent whereas HCl is present in excess.

294 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> produce chlorine = 
$$3 \times 71$$
 g  
58.848 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> would produce chlorine =  $\frac{3 \times 71}{294.0} \times 58.848$  g  
= 42.63 g

**Problem 38.** Gasteric juice contains 3.0 g HCl per litre. If a person produces 2.5 litre of gasteric juice per day, how many antacid tablets containing 400 mg of Al(OH)<sub>3</sub> are needed to neutralise all the acid produced per day? [Dhanbad 1991]

#### Solution:

2.5 litre of gasteric juice contain  $HCl = 2.5 \times 3 = 7.5$  g The desired equation is :

$$\begin{array}{ccc} Al(OH)_3 + & 3HCl \longrightarrow AlCl_3 + 3H_2O \\ & 1 & \text{mole} & 3 & \text{mole} \\ & 78 & g & 3 \times 36.5 & g \end{array}$$

 $3 \times 36.5$  g HCl is completely neutralised by 78 g Al(OH)<sub>3</sub> 7.5 g HCl would be completely neutralised by Al(OH)<sub>3</sub>

$$= \frac{78}{3 \times 365} \times 75 = 5.342 \text{ g}$$

No. of tablets of Al(OH)<sub>3</sub> =  $\frac{5.342}{0.4}$  = 13.36 ≈ 14

**Problem 39.** A mixture of 20 mL of CO, CH<sub>4</sub> and  $N_2$  was burnt in excess of oxygen resulting in reduction of 13 mL by volume. The residual gas was then treated with KOH solution to show a contraction of 14 mL in volume. Calculate volume of CO, CH<sub>4</sub> and  $N_2$  in mixture. All measurements are made at constant pressure and temperature. [I.I.T. 1995]

#### Solution:

Let 'a' mL CO, 'b' mL CH<sub>4</sub> and 'c' mL  $N_2$  be present in the gaseous mixture.

$$a + b + c = 20 \text{ mL}$$
 ... (i)

The desired reactions are:

$$\begin{array}{ccccc} CO + \frac{1}{2}O_2 & \longrightarrow & CO_2 \\ 1 & \text{vol} & 1/2 & \text{vol} & 1 & \text{vol} \\ \text{'a'} & \text{vol} & \text{'a'/2} & \text{vol} & \text{'a'} \text{vol} \\ \end{array}$$

$$\begin{array}{cccc} CH_4 + 2O_2 & \longrightarrow & CO_2 + 2H_2O \\ 1 & \text{vol} & 2 & \text{vol} & 1 & \text{vol} \\ \text{'b'} & \text{vol} & \text{'2b'} & \text{vol} & \text{'b'} \text{vol} \end{array}$$

CO<sub>2</sub> is absorbed by KOH.

Thus, 
$$a + b = 14 \text{ mL}$$
 ... (ii)

From equations (i) and (ii), c = 6 mL, *i.e.*,  $N_2$  in mixt. = 6 mL

$$a + b + c + \text{vol. of } O_2 \text{ taken } - \text{vol. of } O_2 \text{ left } - (a + b) - c$$
  
= 13 mL

or vol. of 
$$O_2$$
 taken – vol. of  $O_2$  left = 13 mL

or vol. of 
$$O_2$$
 used = 13 mL  
or  $\frac{a}{2} + 2b = 13$ mL  
or  $a + 4b = 26$  mL ... (iii)

Solving equations (ii) and (iii),

$$a = 10 \text{ mL}, b = 4 \text{ mL}$$

Vol. of CO = 10 mL; vol. of  $CH_4 = 4$  mL; vol. of nitrogen = 6 mL.

**Problem 40.** A mixture of ethane  $(C_2H_6)$  and ethene  $(C_2H_4)$  occupies 40 litre at 1.00 atm. and at 400 K. The mixture reacts completely with 130 g of  $O_2$  to produce  $CO_2$  and  $H_2O$ . Assuming ideal gas behaviour, calculate the mole fractions of  $C_2H_4$  and  $C_2H_6$  in the mixture. [I.I.T. 1995]

#### **Solution:**

or

Volume of gaseous mixture at N.T.P. conditions is:

$$V = \frac{40 \times 1}{400} \times \frac{273}{1} = 27.3$$
 litre

Let 'x' litre of  $C_2H_4$  and (27.3 - x) litre of  $C_2H_6$  be present in the mixture.

Mole fraction of 
$$C_2H_4 = \frac{x}{27.3}$$
.  
Mole fraction of  $C_2H_6 = \frac{27.3 - x}{27.3}$ 

The desired equations are:

Total volume of oxygen used

$$= \left\{ 3x + \frac{7}{2}(27.3 - x) \right\} \text{ litre}$$
Mass of oxygen used =  $\frac{(7 \times 27.3 - x)}{2 \times 22.4} \times 32$ 

$$\frac{(7 \times 27.3 - x)}{1.4} = 130 \qquad \text{(Given)}$$

$$191.1 - x = 130 \times 1.4$$

$$x = 9.1$$

Mole fraction of  $C_2H_4 = \frac{9.1}{27.3} = 0.33$ 

Mole fraction of 
$$C_2H_6 = \frac{27.3 - 9.1}{27.3} = 0.66$$

**Problem 41.** Equal masses of mercury and iodine are allowed to react completely to form a mixture of mercurous and mercuric iodides. Calculate the ratio of the masses of mercurous and mercuric iodides formed. [I = 127; Hg = 201]

**Solution:** The required equations are:

**Problem 48.** A precipitate of AgCl and AgBr weighs 0.4066 g. On heating in a current of chlorine, the AgBr is converted to AgCl and the mixture loses 0.0725 g in mass. Find the percentage of chlorine in the original mixture.

#### Solution:

Let the masses of AgCl and AgBr in the original mixture be 'a' gram and 'b' gram respectively.

$$a + b = 0.4066$$
 ...(i)  
AgBr  $\xrightarrow{\text{Cl}_2}$  AgCl  
188 g 143.5 g

188 g AgBr changes to 143.5g AgCl

'b' g AgBr changes to  $=\frac{143.5}{188} \times b$  g AgCl

Total mass of AgCl after conversion

$$= a + \frac{143.5}{188} \times b = (0.4066 - 0.0725)$$

or 
$$a + \frac{143.5b}{188} = 0.3341$$
 ...(ii)

Solving eqs. (i) and (ii),

$$a = 0.1007 \text{ g}$$
  
 $b = 0.3059 \text{ g}$ 

Percentage of chlorine in the original mixture

$$=\frac{35.5\times0.1007\times100}{143.5\times0.4066}=6.13$$

### -••• PRACTICE PROBLEMS -•••-

### **■ Subjective Type Questions**

1. 13.4 g of a sample of a salt Na<sub>2</sub>SO<sub>4</sub>·xH<sub>2</sub>O was found to contain 6.3 g of water. Determine the number of molecules of water of crystallisation.

[Ans. 7 water molecules]

**2.** How much potassium chlorate is needed to obtain 2.4 litre oxygen at N.T.P.?

[Ans. 8.75 g]

**3.** Calculate the volume of carbon dioxide obtained at N.T.P. by heating 8.4 g of sodium bicarbonate.

[Ans. 1.12 litre]

**4.** Calculate the volume of air needed for the combustion of 1 kg of carbon.

[Hint: 100 parts of air contain 21 parts of oxygen by volume.] [Ans. 8888.9 litre]

- 5. What weight of chalk containing 60% CaCO<sub>3</sub> would be required for obtaining 200 litres of CO<sub>2</sub> at N.T.P.?
  [Ans. 1.488 kg]
- 6. How many grams of oxygen will be formed by the action of 12 g of sodium peroxide on water? Calculate also the volume of the gas at N.T.P.

[Ans. 2.462 g, 1.7234 litre]

- 7. Calculate the weight of lime (CaO) that can be obtained by heating 200 kg of limestone which is 93% pure.

  [Ans. 104.16 kg]
- **8.** What weight of zinc will react with dilute H<sub>2</sub>SO<sub>4</sub> to liberate 1000 mL of hydrogen at 27°C and 750 mm pressure? [Zn = 65]

[Ans. 2.6 g of zinc]

**9.** What weight of AgCl will be precipitated when a solution containing 4.77 g of NaCl is added to a solution of 5.77 g of AgNO<sub>3</sub>?

[Hint: AgNO<sub>3</sub> is the limiting reagent in this problem.] [Ans. 4.87 g AgCl]

How much of iron can be theoretically obtained by the reduction of 1 kg of Fe<sub>2</sub>O<sub>3</sub>? [Fe = 56][Ans. 700 g]

11. Caustic soda is often prepared commercially by the reaction of Na<sub>2</sub>CO<sub>3</sub> with slaked lime, Ca(OH)<sub>2</sub>. How many grams of NaOH can be obtained by treating 2 kg of Na<sub>2</sub>CO<sub>3</sub> with Ca(OH)<sub>2</sub>?

[Ans. 1.51 kg]

**12.** Most of the commercial hydrochloric acid is prepared by heating NaCl with concentrated H<sub>2</sub>SO<sub>4</sub>. How much sulphuric acid containing 90% H<sub>2</sub>SO<sub>4</sub> by weight is needed for the production of 1 kg of concentrated hydrochloric acid containing 42.0% HCl by weight?

[Hint: Amount of pure HCl in 1 kg of 42.0% acid is 0.42 kg. Determine the H<sub>2</sub>SO<sub>4</sub> required to produce 0.42 kg HCl. It comes to 0.564 kg. Finally, determine the H<sub>2</sub>SO<sub>4</sub> solution containing 90% H<sub>2</sub>SO<sub>4</sub>.]

[Ans.  $0.6266 \text{ kg H}_2\text{SO}_4 \text{ solution}]$ 

13. Iodine can be made by the reaction,

 $2NaIO_3 + 5NaHSO_3 \rightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2$ To produce 2 kg of iodine, how much NaIO<sub>3</sub> and how much NaHSO<sub>3</sub> must be used ?

[Ans. 3.12 kg NaIO<sub>3</sub>, 4.10 kg NaHSO<sub>3</sub>]

**14.** The reduction of Cr<sub>2</sub>O<sub>3</sub> by Al proceeds quantitatively on ignition by a suitable fuse.

$$2Al + Cr_2O_3 \longrightarrow Al_2O_3 + 2Cr$$

How much metallic chromium can be made by bringing to reaction temperature a mixture of 5.0 kg Al and  $20 \text{ kg Cr}_2\text{O}_3$ . Which reactant remains at the completion of the reaction and how much?

[Ans. 9.6 kg chromium; 5.9 kg Cr<sub>2</sub>O<sub>3</sub>]

- 15. 10 g of FeS is treated with dilute H<sub>2</sub>SO<sub>4</sub> and liberated gas is passed through an aqueous solution of CdCl<sub>2</sub>. The amount of cadmium sulphide precipitated is 14.4 g. Calculate the percentage purity of FeS. [Fe = 56; Cd = 112]
  [Ans. 88% purity]
- 16. 50 mL of a mixture of CO and H<sub>2</sub> gave 20 mL of CO<sub>2</sub> after combustion in excess of air. Determine the percentage of CO by volume in the mixture.
  [Ans. 40%]

17. A colourless gas burns with a blue flame and reduces hot copper oxide to copper. When burnt in oxygen, it produces a gas which turns lime water milky. Calculate the volume of the gas at 100°C and 1.5 atm. pressure when 50 mL of oxygen at N.T.P. is required for complete combustion.

[Ans. The gas is CO, volume = 91.08 mL]

- **18.** What volume of hydrogen measured at 27°C and 776.7 mm pressure would be obtained by treating 1.3 g of pure zinc with excess of hydrochloric acid. Aqueous tension at 27°C is  $26.7 \, \text{mm}$ , [Zn = 65][Ans. 498.86 mL]
- 19. 34 g of pure H<sub>2</sub>O<sub>2</sub> is decomposed. Calculate the weight and volume at N.T.P. of oxygen that will be evolved. [Ans. 16 g, 11.2 litre]
- 20. 6 g of an impure sample of KClO<sub>3</sub> gave 1.9 g of oxygen on strong heating in presence of a catalyst. What is the percentage purity of the sample? [Ans. Percentage purity = 80.9]
- 21. Find the percentage composition of iron and magnesium, 5.0 g, which when dissolved in acid, gave 2.81 litre of  $H_2$  at N.T.P. [Fe = 56; Mg = 24][Ans. Fe = 69.60%; Mg = 30.40%]
- 22. 10 g of an alloy of aluminium and magnesium is treated with excess of dilute HCl. The evolved hydrogen collected over mercury at 0°C has a volume of 1.2 litre at 0.29 atm. pressure. Calculate the percentage composition of the alloy. [Al = 27; Mg = 24][Ans. Al = 54.87%; Mg = 45.13%]
- 23. A mixture of calcium and magnesium carbonates weighing 1.4 g was strongly heated until no further loss of weight was perceived. The residue weighed 0.76 g. What percentage of MgCO<sub>3</sub> was present in the mixture? [Ans. 20.45%]
- 24. A mixture of NaI and NaCl gave with H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> equal in weight to the original mixture taken. Find the percentage composition of the mixture.

[Hint: 
$$2\text{NaI} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HI}$$
  
 $2 \times 150\text{g}$   $142\text{g}$   
 $2\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$   
 $2 \times 58.5 \text{ g}$   $142 \text{ g}$ 

Let 100 g of the mixture be taken 'a' g NaI and (100 - a)g NaCl are present. Quantity of Na2SO4 formed is:

$$\frac{142}{300} \times a + \frac{142}{117} (100 - a) = 100$$
 ]

[Ans. 28.86% NaI; 71.14% NaCl]

- 25. How much potassium chlorate must be strongly heated to get as much oxygen as would be obtained from 10.8 g of mercuric oxide? [K = 39; Cl = 35.5; Hg = 200][Ans. 2.04 g KC1O<sub>3</sub>]
- 26. What will be the ratio of the yields of hydrogen prepared by the action of (i) dilute HCl and (ii) super-heated steam on the same amount of metallic iron? [Ans. The ratio is 3:4.]

27. How many grams of cupric oxide will be completely reduced by hydrogen gas produced from 6.53 g of zinc by boiling it with excess of NaOH solution? [Zn = 65.3; Cu = 63.5]

[Hint: The required reactions are:

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

$$65.3 g \qquad \qquad 2 g$$

$$CuO + H_2 \longrightarrow Cu + H_2O]$$

$$79.5 g \quad 2 g$$

[Ans. 7.95 g]

28. 6 grams of an impure sample of NH<sub>4</sub>Cl were boiled with excess of alkali till all the ammonia was released. The issuing gas was completely neutralised by 20 mL of a dilute H2SO4 solution of specific gravity 1.16 and containing 22.19% of H<sub>2</sub>SO<sub>4</sub> by weight in it. What is the percentage purity of the sample of ammonium chloride?

[**Hint :** Amount of 
$$H_2SO_4 = \frac{22.19}{100} \times 20 \times 1.16 = 5.148 g$$
  
The required equations are :

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$34 \text{ g} \qquad 98 \text{ g}$$

$$NH_3 \text{ neutralised by } 5.148 \text{ g } H_2SO_4 = \frac{34}{98} \times 5.148 = 1.786 \text{ g}$$

$$NH_4Cl + NaOH \longrightarrow NH_3 + NaCl + H_2O$$

NH<sub>4</sub>Cl required to produce 1.786 g NH<sub>3</sub> = 
$$\frac{53.5}{17} \times 1.786$$
  
- 5.62 g

Percentage purity = 
$$\frac{5.62}{6.0} \times 100 = 93.67$$
]

29. 0.5 g of pyrolusite (naturally occurring MnO<sub>2</sub>) were boiled with excess of conc. HCl and the issuing gas was passed through a solution of potassium iodide, when 0.635 g of iodine were liberated. What was the percentage of pure  $MnO_2$  in the pyrolusite sample ? [Mn = 55; Cl = 35.5; K=39; I = 1271

[Hint: Required equations are:

$$\begin{array}{c} MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2 \\ Cl_2 + 2KI \longrightarrow 2KCl + I_2 \end{array}$$

[Ans. 43.5]

i.e.,

**30.** A mixture of cuprous oxide (Cu<sub>2</sub>O) and cupric oxide (CuO) was found to contain 88% copper. Calculate the amount of each oxide in 5 g sample of the mixture. [Cu = 64]

[Hint: Let a g of  $Cu_2O$  and (100 - a) g of CuO be present in 100 g of the mixture. The required equations are:

$$\begin{array}{c} \text{Cu}_2\text{O} + \text{C} \longrightarrow 2\text{Cu} + \text{CO} \\ 144 \text{ g} & 128 \text{ g} \\ \text{CuO} + \text{C} \longrightarrow \frac{\text{Cu}}{64 \text{ g}} + \text{CO} \\ 80 \text{ g} & 64 \text{ g} \\ \end{array}$$

$$\frac{128}{144} \times a + \frac{64}{80}(100 - a) = 88 \qquad \text{(Given } a = 90 \\ a = 90 \\ \text{i.e.,} & \text{Cu}_2\text{O} = 90 \text{ g} \quad \text{and} \quad \text{CuO} = 10 \text{ g} \\ \text{[Ans. Cu}_2\text{O} = 4.5 \text{ g}; \quad \text{CuO} = 0.5 \text{ g}] \end{array}$$

31. 10 mL of a gaseous hydrocarbon were burnt completely in 80 mL of O<sub>2</sub> at N.T.P. The remaining gas occupied 70 mL at N.T.P. The volume becomes 50 mL on treatment with KOH. What is empirical formula of hydrocarbon?

[Hint: 
$$C_xH_y + (x + y/4)O_2 \longrightarrow xCO_2 + y/2H_2O$$
  
1 vol  $(x + y/4)$  vol  $x$  vol  $y/2$  vol  
10 mL  $10(x + y/4)$  mL  $10x$  mL  $zero$   
 $CO_2$  produced  $= (70 - 50) = 20$  mL  
Unreacted oxygen  $= 50$  mL  
Oxygen used  $= 30$  mL  
So,  $10x = 20$  or  $x = 2$   
 $10\left(x + \frac{y}{4}\right) = 30$   
or  $x + \frac{y}{4} = 3$  or  $\frac{y}{4} = 1$  or  $y = 4$ ]  
[Ans.  $C_2H_4$ ]

32. Find the resultant volumes measured at the same temperature and pressure when (i) 10 mL of carbon monoxide are exploded with 25 mL of oxygen and (ii) 10 mL of oxygen are exploded with 25 mL of carbon monoxide.

[Ans. (i) 
$$O_2 = 20 \text{ mL}$$
,  $CO_2 = 10 \text{ mL}$ , (ii)  $CO = 5 \text{ mL}$ ,  $CO_2 = 20 \text{ mL}$ ]

- 33. 12 mL of a gaseous hydrocarbon are exploded with excess of oxygen. The contraction observed is 30 mL. When treated with a solution of KOH, there is further contraction of 24 mL. What is the molecular formula of the hydrocarbon? [Ans. C<sub>2</sub>H<sub>6</sub>]
- 34. 500 mL of a hydrocarbon burnt in excess of oxygen, yield 2500 mL of CO<sub>2</sub> and 3.0 litre of water vapours. All the volumes being measured at the same temperature and pressure. What is the formula of the hydrocarbon?
  [Ans. C<sub>5</sub>H<sub>12</sub>]
- 35. Ca(OH)<sub>2</sub> + 2NH<sub>4</sub>Cl = CaCl<sub>2</sub> + 2NH<sub>3</sub> + 2H<sub>2</sub>O Find from the above equation the amount in grams of NH<sub>4</sub>Cl required to produce 2.024 litre of NH<sub>3</sub> at 750 mm pressure and 0°C. Also find the weight of CaCl<sub>2</sub> produced. [Ans. 4.78 g NH<sub>4</sub>Cl; 4.96 g CaCl<sub>2</sub>]
- 36. 1.4 g of a sample of marble (CaCO<sub>3</sub>) containing silica as impurity, gave 282 mL of carbon dioxide at 15°C and 767 mm pressure, when treated with excess of dilute HCl. Calculate the percentage of impurity in the sample.
  [Ans. Percentage of impurity = 14]
- 37. 60 mL of a mixture of carbon monoxide and hydrogen were mixed with 40 mL of oxygen and the mixture was exploded in an eudiometer. After cooling, the volume was found to be 30 mL. Find the composition of the original mixture. (Volumes are measured at the same temperature and pressure.)

[Hint: Let x mL of CO and (60 - x) mL of H<sub>2</sub> be present in the original mixture.

(i) 
$$2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2$$

$$2 \text{ vol} \quad 1 \text{ vol} \quad 2 \text{ vol}$$

$$x \qquad \frac{x}{2} \qquad x$$
(ii) 
$$2\text{H}_2 + \text{O}_2 \longrightarrow \text{H}_2\text{O}$$

$$2 \text{ vol} \quad 1 \text{ vol} \quad 0 \text{ vol}$$

$$(60 - x) \qquad \frac{(60 - x)}{2} \text{ after cooling}$$

$$\text{Oxygen used} = \frac{x}{2} + \frac{60 - x}{2} = 30 \text{ mL}$$

$$\text{Residual oxygen} = 40 - 30 = 10 \text{ mL}$$

$$\text{Vol of CO}_2 + \text{Residual oxygen} = x + 10 = 30$$

$$\text{or} \qquad \qquad x = 20$$

$$\text{CO'volume} = 20 \text{ mL}; \text{H}_2 \text{ volume} = 40 \text{ mL}$$

- 38. A mixture of marsh gas (CH<sub>4</sub>) and acetylene requires 22 mL of oxygen for complete combustion and produces 14 mL of carbon dioxide. Find the volume of each component in the mixture when all the volumes are measured at N.T.P.

  [Ans. CH<sub>4</sub> = 6 mL; C<sub>2</sub>H<sub>2</sub> = 4 mL]
- 39. 100 mL of a mixture of carbon monoxide, methane and hydrogen are mixed with 300 mL of oxygen and fired. After cooling the resultant gas occupied 285 mL and after absorption by potash 205 mL of oxygen remained. Find the composition of the mixture if all the volumes are measured under the same conditions of temperature and pressure.

  [Ans. CO = 50 mL; CH<sub>4</sub> = 30 mL; H<sub>2</sub> = 20 mL]
- 40. What weight of oxalic acid crystals (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O), on being heated with excess of conc. H<sub>2</sub>SO<sub>4</sub> would give 1 litre of the mixture of gases at N.T.P.? What volume of gaseous product would be obtained at N.T.P. by (i) burning the above mixture of gases and (ii) passing the mixture of gases repeatedly over red hot carbon?

[Ans. 2.81 g; (i) 1 litre (ii) 1.5 litre]

41. Igniting MnO<sub>2</sub> converts it quantitatively to Mn<sub>3</sub>O<sub>4</sub>. A sample of pyrolusite is of the following composition: MnO<sub>2</sub> 80%; SiO<sub>2</sub> and other inert constituents 15% and rest being water. The sample is ignited in air the constant weight. What is the percentage of Mn in the ignited sample?

$$[Mn = 54.9, O = 16]$$

[Hint : First determine the amount of  $Mn_3O_4$  from 80 g of  $MnO_2$ . It comes to 70.2 g. Total residue 70.2 + 15.0 = 85.2 g

% of Mn<sub>3</sub>O<sub>4</sub> in the ignited sample = 
$$\frac{70.2}{85.2} \times 100$$
= 82.4

% of Mn in the ignited sample = 
$$\frac{3 \times 54.9}{228.7} \times 82.4 = 59.36$$
 ]

**42.** A 2.0 g of sample containing Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> loses 0.248 g when heated to 300°C. What is the percentage of Na<sub>2</sub>CO<sub>3</sub> in the mixture?

[Hint: On heating only NaHCO3 is decomposed.]

[Ans. % of  $Na_2CO_3 = 66.4$ ]

43. 25.4 g of iodine and 14.2 g of chlorine are made to react completely to yield a mixture of ICl and ICl<sub>3</sub>. Calculate the number of moles of ICl and ICl<sub>3</sub> formed.

[Hint: 
$$I_2$$
 +  $2Cl_2 \longrightarrow ICl_3$  +  $ICl_3$ ]
254 g 142 g 1 mole 1 mole

[Ans. 0.1 mole IC1<sub>3</sub> and 0.1 mole IC1.]

- 44. 2.68 g of a mixture of CaCO<sub>3</sub>, MgCO<sub>3</sub> and NaHCO<sub>3</sub> suffered a loss of 1.19 g on heating. The residue on treatment with excess of hydrochloric acid gave 0.112 litre of CO<sub>2</sub> as measured at N.T.P. Calculate the weight of each component.
  [Ans. CaCO<sub>3</sub> = 1 g; MgCO<sub>3</sub> = 0.84 g; NaHCO<sub>3</sub> = 0.84 g]
- **45.** Crude calcium carbide is made in electric furnace by the following reaction,

$$CaO + 3C \longrightarrow CaC_2 + CO$$

The product contains 85% CaC<sub>2</sub> and 15% unreacted CaO.

- (a) How much CaO is to be added to the furnace charge for each 1000 kg of CaC<sub>2</sub> (pure)?
- (b) How much CaO is to be added to the furnace charge for each 1000 kg of crude product?

[Hint: (a) For getting 1000 kg pure CaC2, the CaO required  $=\frac{56}{64} \times 1000 = 875 \text{ kg}$ 

Free CaO present = 
$$\frac{15 \times 1000}{85}$$
 = 176.47 kg

Total = 875 + 176.47 = 1051.47 kg

(b) 1000 kg crude product consists 850 kg CaC2 and 150 kg CaO.

CaO required for 850 kg 
$$CaC_2 = \frac{56}{64} \times 850 = 743.75$$
 kg  
Total = 743.75 + 150 = 893.75 kg

46. A fluorine disposal plant was constructed to carry out the reactions.

$$F_2 + 2NaOH \longrightarrow 2NaF + H_2O + \frac{1}{2}O_2$$
  
 $2NaF + CaO + H_2O \longrightarrow CaF_2 + 2NaOH$ 

As the plant operated, excess lime was added to bring about complete precipitation of the fluorides as CaF2. Over a period of operation 2000 kg of fluorine was fed into the plant and 10000 kg of lime was required. What was the percentage utilization of lime?

38 g fluorine require CaO = 56 g

$$2000 \times 1000$$
 g fluorine require CaO =  $\frac{56}{38} \times 2000 \times 1000$   
=  $\frac{56}{19} \times 10^6$  g  
% utilization =  $\frac{56}{19} \times \frac{10^6}{10^7} \times 100 = 29.5$ ]

- 47. 20 mL solution containing 0.20 g of an impure sample of H<sub>2</sub>O<sub>2</sub> reacts with 0.316 g of KMnO<sub>4</sub> in presence of H<sub>2</sub>SO<sub>4</sub>.
  - (i) Find the purity of hydrogen peroxide sample.
  - (ii) Calculate the volume of dry oxygen evolved at 27°C and 750 mm pressure.

[Hint: 
$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4$$
  
 $_{316 \text{ g}}$   $_{170$ 

[Ans. Purity 85%; 124.72 mL]

48. How many kilograms of pure H<sub>2</sub>SO<sub>4</sub> could be obtained from 1 kg of iron pyrite (FeS<sub>2</sub>) according to the following reactions? [Fe = 56]

$$\begin{array}{c} 4\text{FeS}_2 + 11\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2 \\ 2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3 \\ \text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 \end{array}$$

[**Ans.** 1.63 kg]

49. When 60 mL of a mixture of N<sub>2</sub>O and NO were mixed with an equal volume of pure H2 and exploded, 38 mL of N2 were left. Calculate the volume of each gas present in the original

[Ans. 
$$N_2O = 16 \text{ mL}$$
;  $NO = 44 \text{ mL}$ ]

**50.** Carbon disulphide, CS<sub>2</sub>, can be made from byproduct SO<sub>2</sub>. The overall reaction is,

$$5C + 2SO_2 \longrightarrow CS_2 + 4CO$$

How much CS<sub>2</sub> can be produced from 450 kg of waste SO<sub>2</sub> with excess of coke, if the SO<sub>2</sub> conversion is 82%? [Ans. 219 kg]

51. A mixture containing NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> weighed 1.0235 g. The dissolved mixture was reacted with excess of Ba(OH)<sub>2</sub> to form 2.1028 g BaCO<sub>3</sub> by the reactions,

$$Na_2CO_3 + Ba(OH)_2 \longrightarrow BaCO_3 + 2NaOH$$
  
 $NaHCO_3 + Ba(OH)_2 \longrightarrow BaCO_3 + NaOH + H_2O$   
What is the percentage of NaHCO<sub>3</sub> in the mixture?

[Ba = 137]

[Ans. 39.51%]

52. A blackened silver coin weighing 15 g on treatment with HCl vielded 25 mL of H<sub>2</sub>S at 12°C and 775 mm pressure. What percentage of original silver tarnished?

[Ans. 1.57%]

53. Brass is an alloy of copper and zinc. A sample of brass weighing 5.793 g when treated with excess of dilute sulphuric acid gave 324 mL of hydrogen at 20°C and 750 mm pressure. What is the percentage by weight of copper in the alloy? [Hint: Only zinc will react with dilute H<sub>2</sub>SO<sub>4</sub> to give hydrogen] [Ans. 85.025% copper]

54. Polyethylene is obtained according to following sequence of reactions.

$$CaC_2 + H_2O \longrightarrow CaO + C_2H_2$$
  
 $C_2H_2 + H_2 \longrightarrow CH_2 = CH_2$   
 $nCH_2 = CH_2 \longrightarrow (-CH_2 - CH_2 -)_n$ 

Find out the mass of polyethylene which can be obtained from 10 kg of calcium carbide.

[Hint: The mass of polyethylene is same as the mass of ethylene.] [Ans. 4.375 kg]

55. 1.0 g of a mixture of potassium chloride and potassium iodide dissolved in water and precipitated with silver nitrate, gave 1.618 g of silver halides. Calculate the percentage of each in the mixture, [K = 39, Cl = 35.5, I = 127, Ag = 108][Ans. % KCl = 39.6; % KI = 60.4]

50 mL of dry ammonia gas was sparked for a long time in an eudiometer tube over mercury. After sparking the volume becomes 97 mL. The gaseous mixture is washed with water and after drying, the volume becomes 94 mL. This was mixed with 60.5 mL of oxygen and the mixture was burnt. After the completion of the combustion of H<sub>2</sub>, the volume of the residual gas was 48.75 mL. Derive the molecular formula of ammonia.

[Hint: Let the formula be N<sub>x</sub>H<sub>y</sub>.

Thus,

Initial vol. 
$$N_x H_y \Longrightarrow (x/2) \ N_2 + (y/2) \ H_2$$
Initial vol.  $50 \text{ mL}$   $0$   $0$ 
Final vol.  $(50-a) \text{ mL}$   $\frac{ax}{2}$   $\frac{ay}{2}$ 

i.e.,  $(50-a) + \frac{ax}{2} + \frac{ay}{2} = 97$ 

After washing,  $\frac{ax}{2} + \frac{ay}{2} = 94$ 

or  $50-a=3$ 

or  $a=47 \text{ mL}$ 

Thus,  $N_2 = \frac{47x}{2}$  and  $H_2 = \frac{47y}{2}$ 

or 
$$x + y = 4 \qquad \dots(i)$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

$$\frac{47y}{2} \qquad 60.5 \qquad 0$$

$$0 \qquad \left(60.5 - \frac{47y}{4}\right)$$

Residual gases after combustion =  $N_2 + O_2$  left

$$48.75 = \frac{47x}{2} + 60.5 - \frac{47y}{4} \qquad \dots (ii)$$

Solving (i) and (ii),

$$x = 1$$
 and  $y = 3$ 

Formula is NH3.]

- **57.** 3.2 g of a mixture of KNO<sub>3</sub> and NaNO<sub>3</sub> was heated to constant weight which was found to be 2.64 g. What is the % of KNO<sub>3</sub> in mixture?

  [Ans. 44.22%]
- 58. 3 g sample of blue vitriol (CuSO<sub>4</sub>:5H<sub>2</sub>O) were dissolved in water. BaCl<sub>2</sub> solution was mixed in excess to this solution. The precipitate obtained was washed and dried. It weighed 2.82 g. Determine % of SO<sub>4</sub><sup>2-</sup> by weight in sample. [Ans. 38.72%]
- **59.** 0.260 g sample of limestone is dissolved and calcium is precipitated as calcium oxalate CaC<sub>2</sub>O<sub>4</sub>. After filtration and washing the precipitate, its required 20 mL of 0.05 *M* KMnO<sub>4</sub> solution acidified with sulphuric acid to titrate. What is the percentage of CaO in the limestone?

[Hint: 
$$CaCO_3 \longrightarrow CaO \longrightarrow CaC_2O_4$$
  
1 mole 1 mole 2 mole 2 mole 5 mole  $CaC_2O_4 \longrightarrow CaC_2O_4 
[Ans. 53.8%]

**60.** The chromate ion may be present in waste water from a chrome plating plant. It is reduced to insoluble chromium hydroxide, Cr(OH)<sub>3</sub>, by dithionite ion, S<sub>2</sub>O<sub>4</sub><sup>2-</sup> in basic solution according to following equation:

 $3S_2O_4^{2-} + 2CrO_4^{2-} + 2H_2O + 2OH^- \longrightarrow 6SO_3^{2-} + 2Cr(OH)_3$ 200 L of water require 774 g of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. Calculate molarity and normality of  $CrO_4^{2-}$  in waste water.

[**Hint**: Number of moles of  $Na_2S_2O_4 = \frac{774}{174} = 4.448$  mole;

Number of moles of  $CrO_4^{2-} = \frac{2}{3} \times 4.448 = 2.965$  mole]

[Ans. Molarity = 0.0148 M; Normality = 0.0444 N]

- 61. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.69 g of water and no other products. A volume of 10 L (measured at S.T.P.) of this welding gas is found to weigh 11.6 g. Calculate:
  - (i) empirical formula
  - (ii) molar mass of the gas and
  - (iii) molecular formula.

[Ans. (i) CH; (ii)  $26 \text{ g mol}^{-1}$ ; (iii)  $C_2H_2$ ]

**62.** A mixture of FeO and Fe<sub>3</sub>O<sub>4</sub> when heated in air to a constant weight gains 5% in its weight. Find the composition of initial mixture.

[Ans. FeO (20.25%), Fe<sub>3</sub>O<sub>4</sub> (79.75%)]

63. Superphosphate of lime can be synthesised as:

$$5Ca_3(PO_4)_2 + 11H_2SO_4 \longrightarrow 4Ca(H_2PO_4)_2 + 2H_3PO_4 + 11CaSO_4$$

- (a) How much H<sub>2</sub>SO<sub>4</sub> is required to convert 2g Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> by this reaction?
- (b) Calculate amount of superphosphate of lime obtained from 2 g of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> by this reaction.

[Ans. (a) 1.39 g; (b) 3.39 g]

- **64.** Trifluoroacetic anhydride (CF<sub>3</sub>CO)<sub>2</sub>O was prepared by treating 100 g of trifluoroacetic acid (CF<sub>3</sub>COOH) with 100 g P<sub>4</sub>O<sub>10</sub>. The anhydride collected weighed 65.6 g. What was the percentage yield?

  [Ans. 71.2%]
- **65.** In the study of thermal decomposition of K<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]; 25 mg of the compound produced 2.24 mg of CO<sub>2</sub> along with FeC<sub>2</sub>O<sub>4</sub> and K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Calculate % yield of carbon dioxide. [Ans. 88.9%]
- **66.** 0.105 mole of  $K_2Cr_2O_7$  are required to oxidise a mixture of XO and  $X_2O_3$  to form  $XO_4$  and  $Cr^{3+}$ . If 0.0817 mole of  $XO_4$  is formed, what is atomic mass of X? Given weight of the original mixture  $(XO + X_2O_3)$  is 2.180 g.

[Hint: Involved reactions are:

- (i)  $6XO + 5Cr_2O_7^{2-} + 34H^+ \longrightarrow 6XO_4^- + 10Cr^{3+} + 17H_2O$ (ii)  $3X_2O_3 + 4Cr_2O_7^{2-} + 26H^+ \longrightarrow 6XO_4^- + 8Cr^{3+} + 13H_2O$ [Ans. 100]
- 67. If 20 g CaCO<sub>3</sub> is treated with 20 g HCl, how many grams of CO<sub>2</sub> can be generated according to the following equation, CaCO<sub>3</sub>(s) + 2HCl(aq.) → CaCl<sub>2</sub>(aq.) + H<sub>2</sub>O(l) + CO<sub>2</sub>(g) Which one of the two reactants is limiting?

  [Ans. 8.8 g CO<sub>2</sub>; CaCO<sub>3</sub> is limiting.]
- **68.** Calculate percentage yield if the reaction of 64 g of NaBH<sub>4</sub> with iodine produced 15 g BI<sub>3</sub>.

$$NaBH_4 + 4I_2 \longrightarrow BI_3 + NaI + 4HI$$

[Ans. 2.27%]

**69.** Silver may be removed from solutions of its salts by reaction with metallic zinc according to the reaction,

$$Zn + 2Ag^{+} \longrightarrow 2Ag + Zn^{2+}$$

A 50 g piece of zinc was thrown into a 100 L vat containing 3.0 g Ag<sup>+</sup>/L.

- (a) Which reactant was completely consumed?
- (b) How much of the other substance remained unreacted?
   [Ans. (a) Zinc is completely consumed, (b) 140 g Ag<sup>+</sup> remain unreacted.
- 70. A particular 100 octane aviation gasoline used 1.00 mL of tetraethyllead, (C<sub>2</sub>H<sub>4</sub>)<sub>4</sub>Pb, of density 1.66 g/mL per litre of product. This compound is made as follows:

$$4C_2H_5Cl + 4NaPb \longrightarrow (C_2H_5)_4Pb + 4NaCl + 3Pb$$

How many gram of ethyl chloride is needed to make enough tetraethyllead for 1 L of gasoline?

[Atomic mass of Pb = 207]

[Hint: The mass of 1 mL  $(C_2H_5)_4Pb = 1 \times 1.66 = 1.66$  g. This is the amount needed per litre.]

[Ans.  $1.33 \text{ g C}_2\text{H}_5\text{Cl}$ ]

71. (a) How much bismuth nitrate, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O would be formed from a solution of 15 g bismuth in nitric acid?

$$Bi + 4HNO_3 + 3H_2O \longrightarrow Bi(NO_3)_3 \cdot 5H_2O + NO$$

(b) How much 30% nitric acid (containing 30% HNO<sub>3</sub> by mass) is required to react with this amount of bismuth? [Atomic mass of bismuth = 209]

[Ans. (a) 34.8 g, (b) 60.3 g solution]

72. The roasting of 100 g copper ore yielded 75.4 g of 89.5% pure copper. If the ore is composed of Cu<sub>2</sub>S and CuS with 11 % inert impurity, calculate the % of Cu<sub>2</sub>S in the ore. The equations are:

and 
$$Cu_2S + O_2 \longrightarrow 2Cu + SO_2$$
  
 $CuS + O_2 \longrightarrow Cu + SO_2$ 

[Atomic mass of copper = 63.54]

[Hint: Mass of pure copper from 100 g of copper ore

$$= \frac{75.4 \times 89.5}{100} = 67.483$$
Number of moles =  $\frac{67.483}{63.54} = 1.06$  mole Cu

In the sample, let x per cent  $Cu_2S$  and (89.0 - x) per cent CuS be present.

then, 
$$\frac{2x}{159.15} + \frac{(89.0 - x)}{95.61} = 1.06$$
]  
[Ans. Cu<sub>2</sub>S = 62%.]

73. 150 g of marble chips are dropped into one kilogram of solution of hydrochloric acid containing one tenth of its weight of the pure acid. How much chips will remain undissolved? What weight of anhydrous calcium chloride, and what weight of carbon dioxide gas would be obtained from it?

[Ans. Marble chips left undissolved = 13.014 g; CaCl<sub>2</sub> formed = 152.054 g; CO<sub>2</sub> evolved = 60.24 g]

74. Hydrogen is generated by the action of steam on hot magnesium. Calculate the mass of magnesium that will be required to produce just sufficient hydrogen to combine with all the oxygen that can be obtained by the complete decomposition of 24.5 g of KClO<sub>3</sub>.

[Ans. 14.4 g]

75. The maximum mass of copper sulphate crystals, CuSO<sub>4</sub>·5H<sub>2</sub>O obtained from 20 g of a sample of brass containing only zinc and copper is 37.2 g. What mass of zinc was present in 20 g of brass?

[Atomic masses of Cu = 63.5; S = 32; Zn = 65] [Ans. 10.53 g]

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. The oxygen obtained by the decomposition of 72 g  $\rm H_2O$  is :

[P.M.T. (Rai.) 2005]

(a) 72 g

(b) 46 g

(c) 50 g

(d) 64 g

Ans. (d)

[Hint: 
$$2H_2O(g) \longrightarrow 2H_2(g) + O_2$$
2 mole
36  $g$ 
1 mole

- : 36 g H<sub>2</sub>O give 32 g O<sub>2</sub> on decomposition
- ∴ 72 g H<sub>2</sub>O will give 64 g O<sub>2</sub> on decomposition]
- 2. 35.4 mL of HCl is required for the neutralization of a solution containing 0.275 g of sodium hydroxide. The molarity of hydrochloric acid is: [P.M.T. (Raj.) 2005]
  - (a) 0.97 M
- (b) 0.142 M
- (c) 0.194 M
- (d) 0.244 M

Ans. (c)

[Hint : Number of moles of NaOH =  $\frac{0.275}{40}$  =  $6.875 \times 10^{-3}$ 

Neutralization reaction:

 $HCl(aq.) + NaOH(aq.) \longrightarrow NaCl(aq.) + H_2O(l)$ 

Number of moles of HCl required for neutralization = no. of moles of NaOH

$$= 6.875 \times 10^{-3}$$

Number of moles = 
$$\frac{MV}{1000}$$

$$6.875 \times 10^{-3} = \frac{M \times 35.4}{1000}$$

M = 0.194 M

3. 2.76 g of silver carbonate on being strongly heated yield a residue weighing:

(a) 2.16 g

- (b) 2.48 g
- (c) 2.64 g
- (d) 2.32 g

Ans. (a)

[Hint: 
$$Ag_2CO_3(s) \longrightarrow 2Ag(s) + CO_2(g) + \frac{1}{2}O_2(g)$$
  

$$\begin{array}{ccc}
1 \text{ mole} & 2 \text{ mole} \\
276 \text{ g} & 2 \times 108 \\
& -216 \text{ g}
\end{array}$$

Residue obtained by heating 276 g of  $Ag_2CO_3 = 216$  g

- $\therefore$  Residue obtained by heating 2.76 g of Ag<sub>2</sub>CO<sub>3</sub> =  $\frac{216}{276} \times 2.76$
- 4. 'X' grams of CaCO<sub>3</sub> was completely burnt in air. The mass of solid residue formed is 28 g. What is the value of 'X' (in grams)?

  [E.A.M.C.E.T. (Engg.) 2005]
  - (a) 44

(b) 200

(c) 150

(d) 50

Ans. (d)

[Hint: 
$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$\begin{array}{ccc}
1 & \text{mole} & 1 & \text{mole} \\
100 & g & 56 & g
\end{array}$$

Residue formed by 100 g of CaCO<sub>3</sub> on decomposition = 56 g

Residue formed by 'X' g of CaCO<sub>3</sub> on decomposition = 28 g

$$\frac{56}{100} \times X = 28$$
$$X = 50 \text{ g } 1$$

- 5. 10 grams of CaCO<sub>3</sub> is completely decomposed to X and CaO. X is passed through an aqueous solution containing one mole of sodium carbonate. What is the number of moles of sodium bicarbonate formed? [E.A.M.C.E.3. 2004]
  - (a) 0.2

(b) 0.1

(c) 0.01

(d) 10

$$\begin{array}{ccc} \text{CaCO}_3 & \longrightarrow & \text{CaO} & + & \text{CO}_2 \\ \text{1 mole} & & \text{1 mole} & & (X) \\ 0.1 \text{ mole} & & & 1 \text{ mole} \\ & & & 0.1 \text{ mole} \end{array}$$

Number of moles of 
$$CaCO_3 = \frac{10}{100} = 0.1$$
  
 $Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$  ]

1 mole
0.1 mole
0.2 mole
0.2 mole

- 6. When 32.25 g of ethyl-chloride is subjected to dehydrohalogenation reaction, the yield of the alkene formed is 50%. The mass of the product is:
  - (a) 14 g

(c) 64.5 g

Ans. (d)

[Hint: 
$$CH_3$$
— $CH_2$ — $Cl$  — $CH_2$ — $CH_2$ + $HCl$  1 mole 64.5 g 28 g 32.25 g 14 g

Since, the yield is 50%, the actual mass of the product is 7 g.]

- 7. If 30 mL of H<sub>2</sub> and 20 mL of O<sub>2</sub> react to form water. What is left at the end of the reaction? [A.F.M.C. 2005]
  - (a)  $10 \,\mathrm{mL}\,\mathrm{of}\,\mathrm{H}_2$
- (b)  $5 \text{ mL of } H_2$
- (c)  $10 \,\mathrm{mLof} \,\mathrm{O}_2$
- (d) 5 mL of  $O_2$

Ans. (d)

Thus, 15 mL of O<sub>2</sub> is used up, hence 5 mL of O<sub>2</sub> is left at the end of the reaction.]

- 8. 100 mL of NaOH is neutralised by 10 mL of  $0.5 M H_2SO_4$ . The molarity of NaOH solution will be :
  - (a) 1

(b) 0.1

(c) 0.01

(d) 0.001

Ans. (b)

[Hint: 
$$2 \text{NaOH} + \text{H}_2 \text{SO}_4 \longrightarrow \text{Na}_2 \text{SO}_4 + 2 \text{H}_2 \text{O}_4$$
  

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$\frac{M_1 \times 100}{2} = \frac{0.5 \times 10}{1}$$

$$M_1 = \frac{0.5 \times 10 \times 2}{100} = 0.1$$

- 9. Assuming that petrol is iso-octane (C<sub>8</sub>H<sub>18</sub>) and has a density of 0.8 g mL<sup>-1</sup>, 1.425 L petrol on complete combustion will consume how much of oxygen gas at S.T.P.?
  - (a) 50 L

- (b) 125 L
- (c) 125 mole
- (d) 50 mole

Ans. (c)

[Hint: Mass of petrol =  $1425 \times 0.8 = 1140 \text{ g}$ 

Number of moles of iso-octane = 
$$\frac{1140}{114}$$
 = 10

$$C_8H_{18} + \frac{25}{2}O_2 = 8CO_2 + 9H_2O$$
]

1 mole 12.5 mole
10 mole 125 mole

- 10. Conversion of oxygen to ozone occurs to the extent of 15% only. The mass of ozone that can be prepared from 67.2 L of oxygen at S.T.P. will be:
  - (a) 14.4 g

(b) 96 g

(c) 640 g

(d) 64 g

Ans. (a)

[Hint: Number of moles of  $O_2 = \frac{67.2}{22.4} = 3$   $3O_2 = 2O_3$ 3 mole 2 mole

Since, percentage yield is 15%, number of moles of ozone formed actually from 3 moles of oxygen

$$=\frac{2\times15}{100}$$
 = 0.3 mole

Mass of ozone formed =  $0.3 \times 48 = 14.4$  g]



# **OBJECTIVE QUESTIONS**



**Note:** Choose the correct answer out of the given alternatives in each question.

1.	The percentage of nitrogen in urea is about:			
	(a) 38.4	1	(a) some ny aregon remains uncombined	
_	(c) 59.1	11.	If a mixture containing 3 mole of hydrogen and 1 mole	
2.	The mass of sulphuric acid needed to dissolve 3 g	1	nitrogen is converted completely into ammonia, the ratio	
	magnesium carbonate is:		initial and final volumes under the same temperature at	nd
	(a) $3.5 \mathrm{g}$ $\square$ (b) $7.0 \mathrm{g}$ $\square$		pressure would be:	_
	(c) $1.7 \mathrm{g}$		_ (-) - (-)	
3.	The haemoglobin from red corpuscles of most mammals		— (c) 2.1	
	contain approximately 0.33% of iron by mass. The molecular	12.	The mass of residue left after strongly heating 1.38 g of silv	/er
	mass of haemoglobin is 67200. The number of iron atoms in	1	carbonate will be:	
	each molecule of haemoglobin is:		(a) $1.16 \mathrm{g}$	
	(a) 1		_ (-)	
	(c) 3	13.	100 mL of PH <sub>3</sub> when decomposed produces phosphorus a	nd
4.	10 mL of a solution of H <sub>2</sub> O <sub>2</sub> liberated 0.5 g of I <sub>2</sub> from KI		hydrogen.The change in volume is:	
	solution. The percentage of $H_2O_2$ in the solution is:		(a) 100 mL decrease $\Box$ (b) 100 mL increase	
	(a) 0.27	1 .	(c) 50 mL increase	
	(c) 0.47	14.	7.46 g of KCl are heated in excess of H <sub>2</sub> SO <sub>4</sub> and MnO <sub>2</sub> . T	he
	[Hint: $2KI + H_2O_2 \longrightarrow 2KOH + I_2$ ]		gas evolved is passed through KI solution. The amount	of
_	34 g $2 \times 127$ g	1	iodine set free will be:	
5.	The mass of CO <sub>2</sub> obtained when 60 g of calcium carbonate	1	(a) $12.7 \text{ g}$	
	is treated with excess of hydrochloric acid is:		(c) $6.4 \mathrm{g}$	
	(a) 30.0		[Hint: $[KC1 + H_2SO_4 \longrightarrow K_2SO_4 + 2HC1] \times 2$	
6	_ (-)		$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$	
6.	The quantity of ammonium sulphate necessary for the	-	$2KI + Cl_2 \longrightarrow 2KCl + I_2$	-
	production of ammonia gas sufficient to neutralise a		$2KCl + MnO2 + 2KI \longrightarrow 2K2SO4 + 2KCl + MnCl2 + I2$	
	solution containing 292 g of HCl is: (a) 272 g	15	$2 \times 74.5 \text{ g}$ $2 \times 127$	-
		15.	If 0.5 mole of BaCl <sub>2</sub> is mixed with 0.20 mole of Na <sub>3</sub> PO <sub>4</sub> . T	
	(c) $528 g$ $\Box$ (d) $1056 g$ $\Box$ [Hint: $NH_3 + HC1 \longrightarrow NH_4C1$ and $(NH_4)_2SO_4 = 2NH_3$ ]	}	maximum number of moles Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> that can be formed in	_
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(a) 0.10	
7.				
	is:	16	[Note: Na <sub>3</sub> PO <sub>4</sub> is a limiting reagent.]	
	(a) 23.48	16.	2 2 2	me
	(c) 53.78	ĺ	of resulting gas is:	_
8.	The volume of oxygen required for complete oxidation of 2.0			
	litre of methane at N.T.P. is:		_ (-,	
	(a) 4 litre $\Box$ (b) 12.25 litre $\Box$	17.	1 2	om
	(c) 1 litre $\Box$ (d) 3 litre $\Box$		temperature. The final mixture of gases is:	_
9.	The % loss in mass after heating a pure sample of potassium	-		
	chlorate will be:		(c) $30 \mathrm{mL}$	
	(a) 12.25	18.	12 g of magnesium (At. mass = $24$ ) will react with an acid	l to
	(c) 39.17		give:	
	[Hint: $2KClO_3 \longrightarrow 2KCl + 3O_2$ ]	1	(a) one mole of $H_2$ $\square$ (b) one mole of $O_2$	
	2 × 122.5 g 2 × 74.5		(c) one-half mole of $H_2$ $\square$ (d) one-half mole of $O_2$	
10.	Three volumes of hydrogen are required to combine with one	19.	The mass of quick lime obtained by strongly heating 25 g	g of
	volume of nitrogen to form 2 volumes of ammonia. When		marble is:	
	one mole of hydrogen is allowed to react with one mole of		(a) 14 g	
	nitrogen, the two gases:		(c) 42 g	
	(a) do not combine	20.	A metal oxide is reduced by heating it in a stream	of
	(b) $2/3$ mole of nitrogen remains unreacted		hydrogen. It is found that after complete reduction, 3.15 g	g of

	the oxide has yielded 1.05 g of the metal. We may deduce that:	31.	Volume of oxygen needed for complete combustion of 20 mL of a hydrocarbon $C_xH_v$ will be:
	(a) the atomic mass of the metal is 8 $\Box$		(a) $(x + y/4)$ mL $\Box$ (b) $20(x + y/4)$ mL $\Box$
	(b) the atomic mass of the metal is 4		(c) $1/20(x+y/4)$ mL $\Box$ (d) none of these $\Box$
	(c) the equivalent mass of the metal is 8	32.	Hydrogen evolved at N.T.P. on complete reaction of 27 g of
	(d) the equivalent mass of the metal is 4		aluminium with excess of aqueous NaOH would be:
21			(a) 22.4 litre
21.	The mass of oxygen with which 13.5 g of aluminium will		(c) $67.2$ litre $\Box$ (d) $33.6$ litre $\Box$
	completely react, is:		[Hint: $2AI + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$ ]
	(a) 4 g	33.	The volume of Cl <sub>2</sub> obtained when 4.35 g MnO <sub>2</sub> react
	(c) 12 g	55.	completely with concentrated HCl (At. mass of Mn = 55):
22.	1.6 g of an organic compound on combustion gave 4.4 g		(a) $4.48$ litre $\Box$ (b) $2.24$ litre $\Box$
	carbon dioxide. The % of carbon in organic compound is:		(c) 1.12 litre $\Box$ (d) 0.56 litre $\Box$
	(a) 30	34.	Cyclohexanol is dehydrated to cyclohexene on heating with
	(c) 60		conc. $H_2SO_4$ . If the yield of the reaction is 75%, how much
23.	At N.T.P., 10 litre of hydrogen sulphide gas reacted with 10		cyclohexene will be obtained from 100 g of cyclohexanol?
	litre of sulphur dioxide gas. The volume of gas, after the		(a) 61.5 g
	reaction is complete, would be:		(c) 20.0 g
	(a) 5 litre		[Hint: $C_6H_{11}OH \xrightarrow{-H_2O} C_6H_{10}$ ]
	(c) 15 litre $\Box$ (d) 20 litre $\Box$		100 g 82 g
24.	A substance contains 0.25% iron by mass. The molecular	35.	1 g of Mg is burnt in a closed vessel which contains 0.5 g of
	mass of substance is 89600. The number of iron atoms per		oxygen. The mass of excess reactant is:
	molecule of the substance is:		(a) $0.25 \text{ g of Mg}$ $\square$ (b) $0.33 \text{ g of O}_2$ $\square$
-	(a) 5 (b) 4		(c) $0.1 \text{ g of Mg}$ $\square$ (d) $0.25 \text{ g of O}_2$ $\square$
25	(c) 3	36.	When 1 g of zinc is treated separately with excess of H <sub>2</sub> SO <sub>4</sub>
25.	The minimum amount of hydrogen required to reduce 7.95 g		and excess of NaOH, the ratio of volume of H <sub>2</sub> evolved is:
	of CuO (Mol. mass 79.5) will be:		(a) 1:1
	(a) 2 g		(c) $2:1$
00	(c) 2240 mL at N.T.P.	37.	The mass of CaO required to remove the hardness of 10 <sup>6</sup>
26.	2.0 g mixture of sodium carbonate and sodium bicarbonate		litre of water containing 1.62 g of calcium bicarbonate per
	on heating to constant weight gave 224 mL of CO <sub>2</sub> at N.T.P.		litre is :
	The % weight of sodium bicarbonate in the mixture is:		(a) 140 kg
	(a) 50	20	(c) 420 kg
27	(c) $80$ $\square$ (d) $84$ $\square$ What volume of hydrogen at N.T.P. will be liberated when	38.	The minimum quantity of H <sub>2</sub> S in grams needed to precipitate
21.	3.25 g of zinc completely dissolve in dilute HCl? (At. mass		63.5 g of copper ions will be nearly:
	of $Zn = 65$ )		(a) 63.5 g
	(a) 1.12 litre	30	(c) $31.75 \mathrm{g}$ $\Box$ (d) $20.0 \mathrm{g}$ $\Box$ If 2 moles of $\mathrm{C_2H_5OH}$ completely burn to $\mathrm{CO_2}$ and water, the
	(c) 2.24 litre	39.	mass of carbon dioxide formed is about:
28.	The volume of oxygen at N.T.P. evolved when 1.70 g of		(a) 88 g
20.	sodium nitrate is heated to a constant mass is:		(c) $44 \text{ g}$ $\Box$ (d) $132 \text{ g}$ $\Box$
	(a) 0.112 litre	40.	The amount of ammonium nitrate that should be decomposed
	(c) 22.4 litre		for getting 22.4 litre nitrous oxide is:
29.	50 g limestone is heated. Quantity of quicklime produced is:		(a) 20 g
	(a) 56 g		(c) 60 g
	(c) 14 g	41.	and the second s
30.	Assuming that petrol is iso-octane ( $C_8H_{18}$ ) and has a density		18 g of water will be:
	of 0.8 g mL <sup>-1</sup> . 1.425 litre of petrol on combustion will		(a) 22.4 litre $\Box$ (b) 5.6 litre $\Box$
	consume:		(c) 11.2 litre
	(a) 100 moles of oxygen	42.	The percentage loss in mass on heating Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O is:
	(b) 124 moles of oxygen □		(a) 25 %
	(c) 150 moles of oxygen		(c) 50 %
	(d) 175 moles of oxygen	43.	One mole of calcium phosphide on reaction with excess
			water gives:

[C.B.S.E. 2007]

(a) one mole of ammonia

	, ( · · · · · · · · · · · · · · · · · ·		
	(a) 1 mole of phosphine		(b) one mole of nitric acid $\Box$
	(b) 2 moles of phosphine		(c) two moles of ammonia
	(c) 2 moles of phosphoric acid		(d) two moles of nitric acid
	(d) 1 mole of phosphorus pentoxide	52.	In a balanced equation,
	[Hint: $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$ ]	}	$H_2SO_4 + xHI \longrightarrow H_2S + yI_2 + zH_2O$
	1 mole 2 mole		The values of $x$ , $y$ and $z$ are: [E.A.M.C.E.T. 2003]
44.	An element 'A' reacts with oxygen to produce A <sub>2</sub> O <sub>3</sub> . 1 g of		(a) $x = 3, y = 5, z = 2$
	'A' produces 1.1596 g of A <sub>2</sub> O <sub>3</sub> . Calculate atomic mass of	,	(c) $x = 8, y = 4, z = 4$ $\square$ (d) $x = 5, y = 3, z = 4$ $\square$
	element 'A' (Atomic mass of oxygen = 15.999 g mol <sup>-1</sup> ):	53.	The volume of oxygen necessary for the complete com-
	(a) 20.70		bustion of 20 L of propane is: [C.P.M.T. 2003]
	(c) 100.2		(a) 40 L
45.	Esterification of benzoic acid takes place as:		(c) 80L
	$C_6H_5COOH + CH_3OH \longrightarrow C_6H_5COOCH_3 + H_2O$	54.	How many moles of magnesium phosphate, Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> will
	Benzoic acid Methanol Methyl benzoate		contain 0.25 mole of oxygen atoms? [A.I.E.E.E. 2006]
	24.4 g benzoic acid reacts with 70 mL CH <sub>3</sub> OH (density = 0.79		(a) $0.02$ $\Box$ (b) $3.125 \times 10^{-2}$ $\Box$ (c) $-1.25 \times 10^{-2}$ $\Box$ (d) $2.5 \times 10^{-2}$ $\Box$
	g mL <sup>-1</sup> ) to produce 21.6 g of methyl benzoate. What will be		$\Box$ (c) $1.25 \times 10^{-2}$ $\Box$ (d) $2.5 \times 10^{-2}$
	the percentage yield of reaction?	1	[Hint: 8 moles oxygen = 1 mole $Mg_3(PO_4)_2$
	(a) 71.5%	}	0.25 mole oxygen will be present = $\frac{1}{8} \times 0.25$ mole
16	(c) 91.7%	ł	= 0.03125  mole
46.	1 mole N <sub>2</sub> and 4 mole H <sub>2</sub> are allowed to react in a vessel and after reaction, H <sub>2</sub> O is added to the vessel. Aqueous solution		$= 3.125 \times 10^{-2} \text{ mole}$
	required 1 mole HCl. Mole fraction of $H_2$ in the gaseous	55.	In the reaction, $As_2S_5 + xHNO_3 \longrightarrow 5H_2SO_4 + yNO_2 +$
	mixture after the reaction is:		$2H_3AsO_4 + 12H_2$ , the values of x and y is:
	_	1	[J.E.E. (Orissa) 2006]
	(a) $\frac{1}{6}$		(a) 40,40
	(c) $\frac{1}{3}$	Ì	(c) $30,30$
47.	2 mole of H <sub>2</sub> S and 11.2 L of SO <sub>2</sub> at S.T.P. react according to		[Hint: $As_2S_5 + 40HNO_3 \longrightarrow 5H_2SO_4 + 40NO_2$
	following equation,		$+ 2H_3AsO_4 + 12H_2$
	$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$	30.	At T(K), 100 litres of dry oxygen is present in a sealed
	What will be the number of moles of sulphur formed in the		container. It is subjected to silent electric discharge, till the volumes of oxygen and ozone become equal. What is the
	reaction?		volumes of oxygen and ozone become equal. What is the volume in litres of ozone formed at $T(K)$ ?
	(a) 1.5		[E.A.M.C.E.T. (Engg.) 2006]
	(c) 11.2	1	(a) 50
48.	3.92 g of ferrous ammonium sulphate crystals are dissolved		(c) 30
	in 100 mL of water, 20 mL of this solution requires 18 mL of		[Hint: Let the volume of $O_2$ converted into ozone be = x litre
	potassium permanganate during titration for complete	,	Volume of ozone formed = $\frac{2x}{3}$ litre
	oxidation. The weight of KMnO <sub>4</sub> present in one litre of the		Volume of oxygen left behind = $(100 - x)$ litre
	solution is: [C.E.T. (Tamil Nadu) 2002]		•
	(a) 34.76 g		$\therefore \frac{2x}{3} = 100 - x$ $x = 60 \text{ litre}$
40	(c) 1.238 g		
49.	30 g of magnesium and 30 g of oxygen are reacted, then the residual mixture contains: [K.C.E.T. 2002]		Thus, ozone formed $\frac{2x}{3} = 40$ litre]
	(a) 60 g magnesium oxide only	57.	2 1 ,
	(b) 40 g magnesium oxide and 20 g of oxygen		density 1.84 g/mL is: [B.V.(Pune) 2006]
	(c) 45 g magnesium oxide and 15 g of oxygen		(a) 1.043 m
	(d) 50 g of magnesium oxide and 10 g of oxygen		(c) 10.43 m
50.			[Hint: Mass of solution = 1840 g
	moles of $H_2O_2$ required is : [A.I.I.M.S. 2004]		Mass of $H_2SO_4 = \frac{93}{100} \times 1000 = 930 \text{ g}$
	1		No. of moles = $\frac{930}{98}$
	(a) $\frac{1}{2}$		Mass of water = $1840 - 930 = 910 \text{ g}$
	(c) $\frac{5}{2}$ $\square$ (d) $\frac{7}{2}$ $\square$		
<i>-</i> 1	2	-	Molality = $\frac{930}{98} \times \frac{1000}{910} = 10.43 \text{ m}$
51.	One mole of magnesium nitride on reaction with excess of	58.	7
	water gives: [A.I.E.E.E. 2004]	(	with one mole of sulphite ion in acidic solution is:

	(a) 4/5	[	[Hint: $2KMnO_4 + 3H_2SO_4 + 5 \mid \longrightarrow K_2SO_4 + 2MnSO_4$
	(c) 1		2 mole COOH
	[Hint: $2MnO_4^- + 6H^+ + 5SO_3^{2-} \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$ ]		5 mole 8H <sub>2</sub> O + 10 CO <sub>2</sub>
59.	If equal volumes of 1M KMnO <sub>4</sub> and 1M K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solutions		$0.5 \text{ L} \times 10^{-2} M = \frac{1}{2} \times \frac{1}{100} = \frac{1}{200} M$
	are allowed to oxidise Fe(II) to Fe(III) in acidic medium then	[	$\frac{0.5 \text{ L} \times 10^{-100} \text{ m} - 2}{2} \times \frac{100^{-200} \text{ m}}{2}$
	Fe(II) oxidised will be: [E.A.M.C.E.T. (Med.) 2007]		KMnO <sub>4</sub> reqd. = $\frac{2}{5} \times \frac{1}{200} = \frac{2}{1000} = \frac{20}{10000} = 20 \times 10^{-4} \text{ M}$
	(a) more by $KMnO_4$ $\Box$ (b) more by $K_2Cr_2O_7$ $\Box$	67.	250 mL of a Na <sub>2</sub> CO <sub>3</sub> solution contains 2.65 g of Na <sub>2</sub> CO <sub>3</sub> .
	(c) equal in both the cases	".	10 mL of this solution is added to $x$ mL of water to obtain
	(d) cannot be determined	ļ	$0.001 M \text{ Na}_2\text{CO}_3$ solution. The value of x is:
60.	A gas has a vapour density 11.2. The volume occupied by		(Mol. mass of $Na_2CO_3 = 106$ ) [B.H.U. 2008]
	1 g of the gas at NTP is: [P.M.T.(Pb.) 2005]	}	(a) 1000
	(a) 1L		(c) 9990
	(c) 22.4L		[Hint: 1000 mL of solution contains sodium carbonate
	[Hint: Mol. mass of the gas = $11.2 \times 2 = 22.4$ ]		$= 2.65 \times 4$
61.	The mass of carbon anode consumed (giving only carbon		= $10.60 \text{ g}$ , <i>i.e.</i> , the solution is $0.1 M$
	dioxide) in the production of 270 kg of aluminium metal from		$10 \times 0.1 = 0.001 \times V, i.e., V = 1000$
	bauxite by Hall process is: [C.B.S.E. (P.M.T.) 2005]		x = 1000 - 10 = 990
	(a) $270  \text{kg}$	68.	40 g of a sample of carbon on combustion left 10% of it
	(c) $90 \text{ kg}$ $\square$ (d) $180 \text{ kg}$ $\square$		unreacted. The volume of oxygen required at S.T.P. for this
	[Hint: $2A1_0O_0 + 3C \longrightarrow 4A1_0 + 3CO_0$ ]		combustion reaction is: [E.A.M.C.E.T. (Med.) 2008]
	[Hint: $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$ ] $(3 \times 12)g \longrightarrow (4 \times 27)g$		(a) 22.4L
62.	Sodium bicarbonate on heating decomposes to form sodium		(c) 11.2L
٠	carbonate, CO <sub>2</sub> and water. If 0.2 mole of sodium bicarbonate	69.	The value of 'n' in the reaction is:
	is completely decomposed, how many moles of sodium		$Cr_2O_7^{2-} + 14H^+ + nFe^{2+} \longrightarrow 2Cr^{3+} + nFe^{3+} + 7H_2O$
	carbonate is formed? [C.E.T. (J&K) 2006]		[P.E.T. (M.P.) 2008]
	(a) 0.1		(a) 2
	(c) 0.05		(c) 6
			[ <b>Hint</b> : $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} + 6Fe^{3+} + 7H_2O$ ]
	[Hint: $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$ ]	70.	For the reaction,
63.	How many moles of lead (II) chloride will be formed from a	1	$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$
	reaction between 6.5 g of PbO and 3.2 g HCl? [C.B.S.E. 2008]		the volume of CO required to reduce one mole of Fe <sub>2</sub> O <sub>3</sub> is:
	(a) 0.011		[C.E.T. (Karnataka) 2008]
	(c) 0.044	1	(a) $67.2  \text{dm}^3$
	[ <b>Hint</b> : PbO + 2HCl $\longrightarrow$ PbCl <sub>2</sub> + H <sub>2</sub> O ]	1	(c) $22.4 \mathrm{dm}^3$ $\square$ (d) $44.8 \mathrm{dm}^3$ $\square$
	[Hint: PbO + 2HCl $\longrightarrow$ PbCl <sub>2</sub> + H <sub>2</sub> O ] $\xrightarrow{6.5}$ mole $\xrightarrow{3.2}$ mole	71.	
	[Hint: PbO + 2HCl $\longrightarrow$ PbCl <sub>2</sub> + H <sub>2</sub> O ] $\frac{6.5}{224}$ mole $\frac{3.2}{36.5}$ mole $= 0.029 = 0.087$	71.	The molarity of NaOH solution by dissolving 4g of it in
64.	$\frac{6.5}{224} \text{ mole} \qquad \frac{3.2}{36.5} \text{ mole} \\ = 0.029 \qquad = 0.087$	71.	The molarity of NaOH solution by dissolving 4g of it in 250 mL water is: [J.E.E. (W.B.) 2010]
64.	$\frac{6.5}{224} \text{ mole} \qquad \frac{3.2}{36.5} \text{ mole}$ $= 0.029 \qquad = 0.087$ The number of moles of oxygen is obtained by electrolytic	71.	The molarity of NaOH solution by dissolving 4g of it in 250 mL water is: [J.E.E. (W.B.) 2010]
64.	$\frac{6.5}{224} \text{ mole} \qquad \frac{3.2}{36.5} \text{ mole} \\ = 0.029 \qquad = 0.087$	71.	The molarity of NaOH solution by dissolving 4g of it in 250 mL water is : [J.E.E. (W.B.) 2010] (a) $0.4 \text{ M}$
64.	$\frac{6.5}{224} \text{ mole} \qquad \frac{3.2}{36.5} \text{ mole}$ $= 0.029 \qquad = 0.087$ The number of moles of oxygen is obtained by electrolytic decomposition of 108 g water is: [J.I.P.M.E.R. 2008]		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is: [J.E.E. (W.B.) 2010] (a) $0.4 \mathrm{M}$
64.	$\frac{6.5}{224} \text{ mole} \qquad \frac{3.2}{36.5} \text{ mole}$ $= 0.029 \qquad = 0.087$ The number of moles of oxygen is obtained by electrolytic decomposition of 108 g water is: [J.I.P.M.E.R. 2008] (a) 2.5 $\square$ (b) 3.0 $\square$ (c) 5.0 $\square$ (d) 7.5 $\square$		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is : [J.E.E. (W.B.) 2010] (a) $0.4 \mathrm{M}$
64.	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is: [J.E.E. (W.B.) 2010] (a) $0.4 \text{ M}$
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is: [J.E.E. (W.B.) 2010] (a) $0.4 \text{ M}$
<ul><li>64.</li><li>65.</li></ul>	$\frac{6.5}{224} \text{ mole} \qquad \frac{3.2}{36.5} \text{ mole}$ $= 0.029 \qquad = 0.087$ The number of moles of oxygen is obtained by electrolytic decomposition of 108 g water is: [J.I.P.M.E.R. 2008] (a) 2.5 $\qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad$		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is: [J.E.E. (W.B.) 2010]  (a) 0.4 M □ (b) 0.8 M □  (c) 0.2 M □ (d) 0.1 M □  For the chemical reaction,  FeC <sub>2</sub> O <sub>4</sub> + MnO <sub>4</sub> + H <sup>+</sup> → Fe <sup>3+</sup> + Mn <sup>2+</sup> + CO <sub>2</sub> + H <sub>2</sub> O pick up the incorrect statement:  (a) The sum of coefficients of reactants is equal to that of the products. □
	$\frac{6.5}{224} \text{ mole} \qquad \frac{3.2}{36.5} \text{ mole}$ $= 0.029 \qquad = 0.087$ The number of moles of oxygen is obtained by electrolytic decomposition of 108 g water is: [J.I.P.M.E.R. 2008] (a) 2.5 $\qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad$		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is:  [J.E.E. (W.B.) 2010]  (a) 0.4 M
	$\frac{6.5}{224} \text{ mole} \qquad \frac{3.2}{36.5} \text{ mole}$ $= 0.029 \qquad = 0.087$ The number of moles of oxygen is obtained by electrolytic decomposition of 108 g water is: [J.I.P.M.E.R. 2008] (a) 2.5 $\qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad$		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is: [J.E.E. (W.B.) 2010]  (a) $0.4 \mathrm{M}$
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is:  [J.E.E. (W.B.) 2010]  (a) 0.4 M
65.	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is: [J.E.E. (W.B.) 2010]  (a) $0.4 \mathrm{M}$
	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is:   [J.E.E. (W.B.) 2010]  (a) 0.4 M
65.	The number of moles of oxygen is obtained by electrolytic decomposition of 108 g water is: [J.I.P.M.E.R. 2008]  (a) $2.5$ $\Box$ (b) $3.0$ $\Box$ (c) $5.0$ $\Box$ (d) $7.5$ $\Box$ [Hint: $2H_2O \longrightarrow 2H_2 + O_2$ ] $2 \mod 2 \times 18 = 36 \text{ g}$ During electrolysis of water, the volume of oxygen liberated is $2.24 \text{ dm}^3$ . The volume of hydrogen liberated under the similar conditions will be: [A.I.I.M.S. 2008]  (a) $2.24 \text{ dm}^3$ $\Box$ (b) $1.12 \text{ dm}^3$ $\Box$ (c) $4.48 \text{ dm}^3$ $\Box$ (d) $0.56 \text{ dm}^3$ $\Box$ Acidified KMnO <sub>4</sub> oxidises oxalic acid to CO <sub>2</sub> . What is the volume (in litres) of $10^{-4} M$ KMnO <sub>4</sub> required to completely		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is:   [J.E.E. (W.B.) 2010]  (a) 0.4 M
65.	The number of moles of oxygen is obtained by electrolytic decomposition of 108 g water is: [J.I.P.M.E.R. 2008]  (a) 2.5 $\Box$ (b) 3.0 $\Box$ (c) 5.0 $\Box$ (d) 7.5 $\Box$ [Hint: $2H_2O \longrightarrow 2H_2 + O_2$ ] $\begin{array}{ccccccccccccccccccccccccccccccccccc$		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is: [J.E.E. (W.B.) 2010]  (a) 0.4 M □ (b) 0.8 M □  (c) 0.2 M □ (d) 0.1 M □  For the chemical reaction,  FeC <sub>2</sub> O <sub>4</sub> + MnO <sub>4</sub> + H <sup>+</sup> → Fe <sup>3+</sup> + Mn <sup>2+</sup> + CO <sub>2</sub> + H <sub>2</sub> O  pick up the incorrect statement:  (a) The sum of coefficients of reactants is equal to that of the products. □  (b) The sum of the coefficients of reactants is 32. □  (c) For each of FeC <sub>2</sub> O <sub>4</sub> , 0.6 mole of KMnO <sub>4</sub> is used. □  (d) Only C and Fe elements are oxidised. □  [Hint: Sum of coefficients  5FeC <sub>2</sub> O <sub>4</sub> + 3MnO <sub>4</sub> + 24H <sup>+</sup> 32
65.	The number of moles of oxygen is obtained by electrolytic decomposition of 108 g water is: [J.I.P.M.E.R. 2008]  (a) 2.5 $\Box$ (b) 3.0 $\Box$ (c) 5.0 $\Box$ (d) 7.5 $\Box$ [Hint: $2H_2O \longrightarrow 2H_2 + O_2$ ] $2 \mod 2 + 10 \mod 2 + $		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is: [J.E.E. (W.B.) 2010]  (a) 0.4 M □ (b) 0.8 M □  (c) 0.2 M □ (d) 0.1 M □  For the chemical reaction,  FeC <sub>2</sub> O <sub>4</sub> + MnO <sub>4</sub> + H <sup>+</sup> → Fe <sup>3+</sup> + Mn <sup>2+</sup> + CO <sub>2</sub> + H <sub>2</sub> O  pick up the incorrect statement:  (a) The sum of coefficients of reactants is equal to that of the products. □  (b) The sum of the coefficients of reactants is 32. □  (c) For each of FeC <sub>2</sub> O <sub>4</sub> , 0.6 mole of KMnO <sub>4</sub> is used. □  (d) Only C and Fe elements are oxidised. □  [Hint: Sum of coefficients  5FeC <sub>2</sub> O <sub>4</sub> + 3MnO <sub>4</sub> + 24H <sup>+</sup> 32
65.	The number of moles of oxygen is obtained by electrolytic decomposition of 108 g water is: [J.I.P.M.E.R. 2008]  (a) 2.5 $\Box$ (b) 3.0 $\Box$ (c) 5.0 $\Box$ (d) 7.5 $\Box$ [Hint: $2H_2O \longrightarrow 2H_2 + O_2$ ] $\begin{array}{ccccccccccccccccccccccccccccccccccc$		The molarity of NaOH solution by dissolving 4g of it in 250 mL water is: [J.E.E. (W.B.) 2010]  (a) 0.4 M □ (b) 0.8 M □  (c) 0.2 M □ (d) 0.1 M □  For the chemical reaction,  FeC <sub>2</sub> O <sub>4</sub> + MnO <sub>4</sub> + H <sup>+</sup> → Fe <sup>3+</sup> + Mn <sup>2+</sup> + CO <sub>2</sub> + H <sub>2</sub> O  pick up the incorrect statement:  (a) The sum of coefficients of reactants is equal to that of the products. □  (b) The sum of the coefficients of reactants is 32. □  (c) For each of FeC <sub>2</sub> O <sub>4</sub> , 0.6 mole of KMnO <sub>4</sub> is used. □  (d) Only C and Fe elements are oxidised. □

An	swers																	
<b>1.</b> (b)	) 2.	(a)	-3.	(d)	4.	(b)	5.	(d)	6.	(c)	7.	(c)	8.	(a)	9.	(c)	10.	(b)
<b>11.</b> (d)	) 12.	(d)	13.	(c)	14.	(a)	15.	(a)	16.	(b)	17.	(b)	18.	(c)	19.	(a)	20.	(d)
<b>21.</b> (c)	22.	(d)	23.	(a)	24.	(b)	25.	(c)	26.	(d)	27.	(a)	28.	(b)	29.	(b)	30.	(a)
<b>31.</b> (b)	32.	(d)	33.	(c)	34.	(a)	35.	(a)	36,	(a)	37.	(d)	38.	(b)	39.	(b)	40.	(d)
<b>41.</b> (c)	) 42.	(b)	43.	(b)	44.	(d)	45.	(b)	46.	(b)	47.	(a)	48.	(d)	49.	(d)	50.	(c)
<b>51.</b> (c)	52.	(c)	53.	(d)	54.	(b)	55.	(a)	56.	(d)	57.	(c)	58.	(b)	59.	(b)	60.	(a)
<b>61.</b> (c)	62.	(a)	63.	(b)	64.	(b)	65.	(c)	66.	(d)	67.	(b)	68.	(b)	69.	(c)	70.	(a)
<b>71.</b> (a)	72.	(b)	•															



### **Objective Questions for IIT ASPIRANTS**



1. What mass of Mg(OH)<sub>2</sub> is required to neutralize 125 mL of

0.136 M hydrochloric acid solution?

(Molar mass of Mg(OH)<sub>2</sub> =  $58.33 \text{ g mol}^{-1}$ )

(a) 0.248 g

(b) 0.496 g

(c) 0.992 g

(d) 1.98 g

[Hint:  $Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$ 

Number of moles of HCl = 
$$\frac{MV}{1000} = \frac{0.136 \times 125}{1000}$$
  
= 0.017

- 2 mole HCl is neutralized by 58.33 g of Mg(OH)<sub>2</sub>
- 0.017 mole HCl will be neutralized by

$$\frac{58.33}{2}$$
 × 0.017 g Mg(OH)<sub>2</sub> = 0.496 g]

- 2. Calculate the mass of ammonia that can be produced from the decomposition of a sample of (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> containing 0.1 g Pt. Molar mass of  $(NH_4)_2$ PtCl<sub>6</sub> is 443.9 g mol<sup>-1</sup>.
  - (a) 0.0811 g

(b) 0.0766 g

(c) 0.0175 g

(d) 0.00766 g

Consider the following data

dei die following data .	•
Element	Atomic mas
$\boldsymbol{A}$	12.01
R	35.5

A and B combine to form a new substance 'X'. If 4 moles of B combines with 1 mole of A to give 1 mole of 'X' then mass of one mole of 'X' is:

(a) 154 g

(b) 74 g

(c) 47.5 g

(d) 166 g

[Hint:  $A + 4B \longrightarrow X$ 

Molar mass of  $X = 12.01 + 4 \times 35.5 = 154 \text{ g mol}^{-1}$ 

Chlorine can be prepared by reacting HCl with MnO<sub>2</sub>. The reaction is represented by this equation:

$$MnO_2(s) + 4HCl(aq.) \longrightarrow Cl_2(g) + MnCl_2(aq.) + 2H_2O(l)$$

Assuming the reaction goes to completion, what mass of concentrated HCl solution (36% HCl by mass) is needed to produce 2.5 g of Cl<sub>2</sub>?

(a) 5.15 g

(b) 14.3 g

- (d) 26.4 g
- 5. What volume of 3M Na<sub>2</sub>SO<sub>4</sub> must be added to 25 mL of 1 M BaCl<sub>2</sub> to produce 5 g BaSO<sub>4</sub>?
  - (a) 7.2 mL

(b) 8.3 mL

(c) 10 mL

(d) 14 mL

[Hint:  $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2NaCl$ 

Number of moles of BaSO<sub>4</sub> = 
$$\frac{\text{Mass}}{\text{Molar mass}}$$
  
=  $\frac{5}{233}$  = 0.0215

Number of moles of  $Na_2SO_4$  needed = 0.0215

$$\frac{MV}{1000} = 0.0215$$
$$\frac{3 \times V}{1000} = 0.0215$$
$$V = 7.2 \text{mL}$$

When FeCl<sub>3</sub> is ignited in an atmosphere of pure oxygen, this reaction takes place:

$$4\text{FeCl}_3(s) + 3\text{O}_2(g) \longrightarrow 2\text{Fe}_2\text{O}_3(s) + 6\text{Cl}_2(g)$$
  
If 3 moles of FeCl<sub>3</sub> are ignited in the presence of 2 moles of O<sub>2</sub> gas, how much of which reagent is present in excess and, therefore, remains unreacted?

- (a) 0.33 mole FeCl<sub>2</sub> remain unreacted
- (b) 0.67 mole FeCl<sub>3</sub> remain unreacted
- (c) 0.25 mole O<sub>2</sub> remain unreacted
- (d) 0.50 mole O<sub>2</sub> remain unreacted
- A self-contained breathing apparatus uses potassium superoxide, KO<sub>2</sub>, to convert the carbon dioxide and water in exhaled air into oxygen, as shown by the equation:

$$4KO_2(s) + 2H_2O(g) + 4CO_2(g) \longrightarrow 4KHCO_3(s) + 3O_2(g)$$
  
How many molecules of oxygen gas will be produced from the 0.0468 g of carbon dioxide that is exhaled in a typical breath?

- (a)  $4.8 \times 10^{20}$
- (b)  $6.4 \times 10^{20}$
- (c)  $8.5 \times 10^{20}$
- (d)  $1.9 \times 10^{21}$

[Hint: : 4 mole CO<sub>2</sub> gives 3 mole O<sub>2</sub>

$$\therefore \left(\frac{0.0468}{44}\right) \text{ mole CO}_2 \text{ will give } \frac{3}{4} \times \frac{0.0468}{44} \text{ mole O}_2$$
$$= 7.977 \times 10^{-4} \text{ mole}$$

Number of molecules of  $O_2 = 7.977 \times 10^{-4} \times 6.023 \times 10^{23}$ 

$$= 4.8 \times 10^{20} \, 1$$

Antimony reacts with chlorine according to this equation:

$$2Sb + 3Cl_2 \rightleftharpoons 2SbCl_3$$

How many grams of SbCl<sub>3</sub> can be prepared if 0.012 mole of antimony are reacted with 0.02 mole of chlorine? The molar mass of SbCl<sub>3</sub> equals  $228.2 \text{ g mol}^{-1}$ :

(a) 1.52 g

(b) 1.83 g

(c) 2.74 g

- (d) 4.56 g
- 9. A gaseous mixture of propane and butane of volume 3L on complete combustion produces 10 L of CO2 under standard conditions of temperature and pressure. The ratio of volumes of propane to butane is:
  - (a) 1:2

(b) 2:1

(c) 3:2

- (d) 3:1
- 10. What amount of silver will be obtained on thermal decomposition of 2.76 g of silver carbonate Ag<sub>2</sub>CO<sub>3</sub> (276 amu)?
  - (a) 2.16 g

(b) 0.216 g

(c) 216 g

- (d) 21.6 g
- 11.  $PH_3(g)$  decomposes on heating to produce phosphorous and hydrogen. The change in volume when 100 mL of such gas is decomposed:
  - (a)  $+50 \,\text{mL}$
- (b)  $+500 \,\text{mL}$
- (c)  $-50 \, \text{mL}$
- (d)  $-500 \,\mathrm{mL}$

[Hint:  $4PH_3(g) \xrightarrow{Heat} P_4(s) + 6H_2(g)$ 

Volume of H<sub>2</sub> formed by decomposition of 100 mL PH<sub>3</sub>

$$=\frac{6}{4} \times 100 = 150 \text{ m}$$

 $= \frac{6}{4} \times 100 = 150 \text{ mL}$ Thus, change in volume = (150 - 100) = 50 mL]

- 12. What amount of BaSO<sub>4</sub> can be obtained on mixing 0.5 mole BaCl<sub>2</sub> with 1 mole of H<sub>2</sub>SO<sub>4</sub>?
  - (a) 0.5 mole
- (b) 0.15 mole
- (c) 0.1 mole
- (d) 0.2 mole

[Hint:  $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$ Initially 0.5 1 0 0 0.5  $2 \times 0.51$ After reaction 0 (1 - 0.5)

13. In the reaction,

 $CrO_5 + H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + H_2O + O_2$ one mole of  $CrO_5$  will liberate how many moles of  $O_2$ ?

(a) 5/2

(b) 5/4

- (d) none of these
- 14. Calcium carbonate decomposes on heating according to the equation:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

At S.T.P. the volume of CO<sub>2</sub> obtained by thermal decomposition of 50 g of CaCO<sub>3</sub> will be:

- (a) 22.4 litre
- (b) 44 litre
- (c) 11.2 litre
- (d) 1 litre
- 15. The volume in litres of CO<sub>2</sub> liberated at S.T.P. when 10 g of 90% pure limestone is heated completely, is:
  - (a) 22.4L

- (b) 2.24L
- (c) 20.16L
- (d) 2.016L

$$[ \text{Hint} : CaCO_3 \longrightarrow CaO + CO_2(g) \\ \text{$\stackrel{1 \text{ mole}}{(100 \text{ g})}$} \qquad \qquad \begin{array}{c} 22.4 \text{ lirre} \\ \text{at S.T.P.} \end{array}$$

$$\therefore$$
 100 g CaCO<sub>3</sub> = 22.4 L CO<sub>2</sub> at S.T.P.

∴ 9 g CaCO<sub>3</sub> 
$$\equiv \frac{22.4}{100} \times 9$$
 L at S.T.P.  
= 2.016 L CO<sub>2</sub> at S.T.P. ]

16. A metal oxide has a formula  $Z_2O_3$ . It can be reduced by hydrogen to give free metal and water. 0.1596 g of the metal requires 6 mg of hydrogen for complete reduction. The atomic mass of the metal is:

(a) 27.9

(b) 159.6

(c) 79.8

(d) 55.8

[Hint: 
$$Z_2O_3 + 3H_2(g) \longrightarrow 2Z + 3H_2O$$

∴ 6 g H<sub>2</sub> gives 2 mole Z

 $\therefore$  6 × 10<sup>-3</sup> g H<sub>2</sub> will give 0.002 mole Z

Number of moles = 
$$\frac{\text{Mass}}{\text{Molar mass}}$$
  

$$0.002 = \frac{0.1596}{\text{Molar mass}}$$

: Molar mass = 
$$\frac{0.1596}{0.002}$$
 = 79.8 g mol<sup>-1</sup>]

17. Chlorine gas can be produced by reacting sulphuric acid with a mixture of MnO2 and NaCl. The reaction follows the equation.

$$2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4$$

---+Cl<sub>2</sub>+2H<sub>2</sub>O

what volume of chlorine can be produced from 1 g of sodium chloride under standard conditions of temperature and pressure?

- (a) 1.915 L
- (b) 19.15 L
- (c) 20.22L
- (d) 0.191 L

[Hint: 2 mole NaCl (117 g)  $\equiv$  1 mole Cl<sub>2</sub> (22.4 L at S.T.P.)

∴ 1 g NaCl will give 
$$\frac{22.4}{117}$$
 L Cl<sub>2</sub> at S.T.P.  
= 0.191 L Cl<sub>2</sub> at S.T.P.

18. 1 mole of a gaseous aliphatic compound,  $C_nH_{3n}O_m$  is completely burnt in an excess of oxygen. The contraction in volume is:

- (a)  $\left(1 + \frac{1}{2}n \frac{3}{4}m\right)$  (b)  $\left(1 + \frac{3}{4}n \frac{1}{4}m\right)$  (c)  $\left(1 \frac{1}{2}n \frac{3}{4}m\right)$  (d)  $\left(1 + \frac{3}{4}n \frac{1}{2}m\right)$

- 19. A mixture of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> was completely burnt in an excess of oxygen, yielding equal volumes of CO<sub>2</sub> and steam. Calculate the percentages of the compounds in the original mixture:
  - (a) 25 % CH<sub>4</sub> and 75% C<sub>2</sub>H<sub>4</sub> (b) 30% CH<sub>4</sub> and 70% C<sub>2</sub>H<sub>4</sub>
  - (c) 75% CH<sub>4</sub> and 25% C<sub>2</sub>H<sub>4</sub> (d) 50% CH<sub>4</sub> and 50% C<sub>2</sub>H<sub>4</sub>

Following questions have more than one correct answer:

- 20. 1.5 g of oxygen is produced by heating KClO<sub>3</sub>. How much KCl is produced in the reaction?
  - (a)  $4.15 \times 10^{-2}$  mole (c)  $1.78 \times 10^{-2}$  mole
- (b) 4.33 g
- (d) 1.33 g
- 21. Calculate the amount of lime that can be produced by heating 100 g of 90% pure limestone:
  - (a) 50.4 g

- (b) 0.98 mole
- (c) 0.9 mole

[Hint: 
$$CaCO_3 \longrightarrow CaO + CO_2$$
  
 $100 \text{ g}$   $56 \text{ g}$   
 $100 \text{ g } CaCO_3 \equiv 56 \text{ g } CaO$ 

:. 90 g CaCO<sub>3</sub> = 
$$\frac{56}{100} \times 90$$
 g CaO, *i.e.*, 50.4 g CaO

Number of moles of CaO = 
$$\frac{50.4}{56}$$
 = 0.9 ]

- 22. In an experiment, following four gases were produced. 11.2 L of which two gases at S.T.P. will weigh 14 g?
  - (a) N<sub>2</sub>O

· (b) NO<sub>2</sub>

(c)  $N_2$ 

- (d) CO
- 23. 2 mole of CO<sub>2</sub> is required to prepare:
  - (a) 336 g of NaHCO<sub>3</sub>
- (b) 168 g of NaHCO<sub>3</sub>
- (c) 462 g of Ca(HCO<sub>3</sub>)<sub>2</sub>
- (d) 162 g of Ca(HCO<sub>3</sub>)<sub>2</sub>
- 24. 8.7 g of pure MnO<sub>2</sub> is heated with an excess of HCl and gas evolved is passed into a solution of KI. Calculate the amount of the iodine liberated:

(Mn = 55, Cl = 35.5, I = 127)

- (a) 0.1 mole
- (b) 25.4 g

(c) 15.4 g

(d) 7.7 g

1. (b) 2. (c) 3. (a) 4. (b) 5. (a) **6.** (a) 7. (a) 8. (c) 9. (b) 10. (a) 11. (a) 12. (a) 13. (d) 14. (c) 15. (d) **16.** (c) 17. (d) 18. (d) 19. (d) 20. (c, d)

21. (a, c) 22. (c, d) 23. (a, b, d) 24. (a, b)

# YPE QUESTIONS



#### **THOUGHT 1**

In a reaction vessel 100 g H<sub>2</sub> and 100 g Cl<sub>2</sub> are mixed and suitable conditions are provided for the following reaction,

$$H_2(g) + Cl_2(g) \xrightarrow{?} 2HCl(g)$$

Quantum yield of this reaction is,  $\phi = 10^5$ .

- 1. Select the correct statement(s) for the above reaction:
  - (a) Presence of light is required for this reaction
  - (b) It is a chain reaction
  - (c) Catalyst is required
  - (d) All of the above
- 2. The limiting reagent in this reaction will be:
  - (a)  $H_2$

(b) Cl<sub>2</sub>

- (d) cannot be predicted
- 3. The actual amount of HCl formed in this reaction is:
  - (a) 102.8 g
- (b) 73 g

- (c) 36.5 g
- (d) 142 g
- 4. The amount of excess reactant remaining:
  - (a) 50 g

(b) 97.2 g

(c) 46 g

- (d) 64 g
- 5. The amount of HCl formed (at 90% yield) will be:
  - (a) 36.8 g
- (b) 62.5 g

(c) 80 g

(d) 92.53 g

#### **THOUGHT 2**

Dissolved oxygen in water is determined by using a redox reaction. Following equations describe the procedure:

- $2\text{Mn}^{2+}(aq.) + 4\text{OH}^{-}(aq.) + \text{O}_{2}(g) \longrightarrow 2\text{MnO}_{2}(s) + 2\text{H}_{2}\text{O}(l)$ I.
- II.  $MnO_2(s) + 2I^-(aq.) + 4H^+(aq.) \longrightarrow Mn^{2+}(aq.) +$

 $I_2(aq.) + 2H_2O(l)$ 

 $2S_2O_3^{2-}(aq.) + I_2(aq.) \longrightarrow S_4O_6^{2-}(aq.) + 2I^{-}(aq.)$ Ш.

- 1. How many moles of  $S_2O_3^{2-}$  are equivalent of each mole of  $O_2$ ?
  - (a) 0.5

(c) 2

- (d) 4
- 2. What amount of I<sub>2</sub> will be liberated from 8 g dissolved oxygen?
  - (a) 127 g

(b) 254 g

(c) 504 g

- (d) 1008 g 3. If  $3 \times 10^{-3}$  mole O<sub>2</sub> is dissolved per litre of water then what will be the molarity of I produced in the given reaction?
  - (a)  $3 \times 10^{-3} M$
- (b)  $4 \times 3 \times 10^{-3} M$
- (c)  $2 \times 3 \times 10^{-3} M$
- (d)  $(1/2) \times 3 \times 10^{-3} M$
- Number of which two chemical species will be same in the given procedure?
  - (a) MnO<sub>2</sub>
- (b)  $I_2$

(c) I

- (d)  $S_2O_3^{2-}$
- 8 mg dissolved oxygen will consume ........ (a)  $5 \times 10^{-4}$  mole Mn<sup>2+</sup>
  - (b)  $2.5 \times 10^{-4}$  mole Mn<sup>2+</sup>
  - (c)  $10^{-3}$  mole Mn<sup>2+</sup>
- (d) 2 mole Mn<sup>2+</sup>

- Thought 1 2. (b) 3. (a) 1. (a, b)
- Thought 2 1. (d)
- 2. (a)
- 3. (b)
- 4. (b)
- 4. (a)
- 5. (d) 5. (a)

### INTEGER ANSWER Type Questions

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. The volume of oxygen required for the complete burning of 4 ml of methane at NTP is:
- 2. How much residue is left after strongly heating 1.28 g of silver carbonate?
- 3. The mass of marble required for the preparation of 2.8 g of quick lime by strong heating is:
- 4. 9.5 g of Mg is burnt in a closed vessel containing 5g of O<sub>2</sub>.
  The mass of excess reagent is:
- 5. The amount of ammonium nitrate that should be decomposed for getting 2.24 litre nitrous oxide is:
- 6. Potassium permanganate in presence of dilute H<sub>2</sub>SO<sub>4</sub> reacts with oxalic acid (anhydrous). Write the balanced equation of the reaction and find out how many moles of oxalic acid are oxidised by 2 moles of KMnO<sub>4</sub>?

### Auswers

1. (8) 
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
1 vol. 2 vol. 8 rd.

2. (1) 
$$Ag_2CO_3 \longrightarrow 2Ag + CO_2 + \frac{1}{2}O_2$$

3. (5) 
$$CaCO_3 \longrightarrow CaO_{56 g} + CO_2$$

4. (2) 
$$2Mg + O_2 \longrightarrow 2MgO$$
;

5g O<sub>2</sub> reacts with 
$$=\frac{48}{32}\times5=7.5$$
 g Mg

5. (8) 
$$NH_4NO_3 \longrightarrow N_2O$$
80 g 22.4 litre

**6.** (5) 
$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

# CHAPTER

# Volumetric Analysis

#### Contents:

- 17.1 Introduction
- 17.2 Methods of Expressing Concentrations of Solutions
- 17.3 Types of Titrations
- 17.4 Determination of Equivalent Mass
- 17.5 Calculations of Volumetric Analysis
- 17.6 To Determine the Amount of Sodium Hydroxide and Sodium Carbonate in a given Mixture
- 17.6.1 To Determine the Amount of Sodium Carbonate and Bicarbonate in a Mixture
- 17.7 Kjeldahl's Process

### 17.1 INTRODUCTION

Many chemical reactions in nature, particularly in living systems, occur in aqueous solutions. Reactions are often carried out in the laboratory in aqueous solutions because these are generally more rapid in solution than when pure solid reactants are mixed. A quantitative analysis is one in which the amount or concentration of a particular species in a sample is determined accurately and precisely.

Volumetric analysis is a quantitative analysis. It involves the measurement of the volume of a known solution required to bring about the completion of the reaction with a measured volume of the unknown solution. The reaction used in volumetric analysis must fulfill the following conditions:

- (i) The chemistry of the reaction should be known and it should be represented by a definite chemical equation.
- (ii) The reaction should be instantaneous and proceed to completion over a fairly wide range of concentrations.
- (iii) There must be means to know the exact state of its completion.

The process of addition of the known solution from the burette to the measured volume of solution of the substance to be estimated until the reaction between the two is just complete, is termed as titration. Thus, a titration involves two solutions:

- (i) Unknown solution: The solution consisting the substance to be estimated is termed unknown solution. The substance is termed titrate.
- (ii) Standard solution: The solution in which an accurately known amount of the reagent (titrant) has been dissolved in a known volume of the solution is termed standard solution. There are two types of reagents (titrants):
- (a) **Primary standards:** These can be accurately weighed and their solutions are not to be standardised before use. Oxalic acid ( $H_2C_2O_4$ · $2H_2O$ ), potassium dichromate ( $K_2Cr_2O_7$ ), silver nitrate (AgNO<sub>3</sub>), copper sulphate (CuSO<sub>4</sub>· $5H_2O$ ), ferrous ammonium sulphate [FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>· $6H_2O$ ], sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>· $5H_2O$ ), etc., are the examples of primary standards.
- (b) Secondary standards: The solutions of these reagents are to be standardised before use as these cannot be weighed accurately. The examples are sodium hydroxide (NaOH), potassium hydroxide (KOH), hydrochloric acid (HCl), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), potassium permanganate (KMnO<sub>4</sub>), iodine, etc.

Law of equivalence: It is applied in all volumetric estimations. According to it, the chemical substances react in the ratio of their chemical equivalent masses.

or  $\frac{\text{Mass of substance } A}{\text{Chemical equivalent mass of } A}$ 

 $= \frac{\text{Mass of substance } B}{\text{Chemical equivalent mass of } B}$ 

or gram equivalent of A = gram equivalent of B or milli-gram equivalent of A = milli-gram equivalent of B

The point at which the amounts of the two reactants are just equivalent is known as **equivalence point** or **end point**. An auxiliary substance which helps in the usual detection of the completion of the titration or equivalence point or end point is termed as **indicator**, *i.e.*, substances which undergo some easily detectable changes at the equivalence point are used as indicators.

## 17.2 METHODS OF EXPRESSING CONCENTRATIONS OF SOLUTIONS

The concentration of a solution can be expressed in various ways:

1. Per cent by mass: The percentage by mass of a solute in a solution is 100 times the mass of the solute divided by the total mass of the solution.

$$\%$$
 Solute =  $\frac{\text{Mass of solutein grams}}{\text{Mass of solutionin grams}} \times 100$ 

Thus, 10% solution of sodium chloride means 10 grams of sodium chloride is present in 100 grams of the solution, *i.e.*, 10 grams of sodium chloride has been dissolved in 90 grams of water.

2. Molarity (Molar concentration): It is a common method for expressing the concentration of solution. It is defined as the number of moles of the solute per litre of the solution.

Molarity = Number of moles of solute

Number of millimoles of the solute

or Molarity = Number of milli - moles of the solute

Number of milli - litres of the solution

or Molarity × Number of litres of solution

or

= Number of moles of solute

or Molarity × Number of milli-litres of solution

= Number of milli-moles of solute

When a solution is diluted by adding more of the solvent, the number of moles does not change. The volume of solution and its concentration do change. Let the initial molarity and volume be  $M_1$  and  $V_1$  and the molarity and volume after dilution be  $M_2$  and  $V_2$  respectively.

 $V_1 \times M_1$  = Number of moles of solute =  $V_2 \times M_2$  $V_1 M_1 = V_2 M_2$  (Molarity equation)

Let w grams of the solute of molecular mass M be dissolved in V litres of solution.

Molarity of the solution = 
$$\frac{w}{M \times V}$$

$$\left[\frac{w}{M}\right]$$
 = No. of gram moles of the solute

or Molarity  $\times M = \frac{w}{V} =$  Strength of the solution where M is molecular mass of solute.

Thus, strength of the solution (g/L) (i.e., No. of grams of the solute per litre)

= Molarity × Molecular mass

Solutions are generally expressed as 1M, 2M, M/2, M/10, M/100, M/1000, etc.

1M = Molar solution = 1 gram mole of the solute per litre of solution

M/2 = Semi-molar solution = 1/2 gram mole of the solute per litre of solution

M/10 = Deci-molar solution = 1/10 gram mole of the solute per litre of solution

M/100 = Centi-molar solution = 1/100 gram mole of the solute per litre of solution

M/1000 = Milli-molar solution = 1/1000 gram mole of the solute per litre of solution

3. Molality: It is defined as the number of gram moles of the solute present in 1 kg of the solvent.

$$Molality = \frac{Number of gram moles of the solute}{Number of kilograms of the solvent}$$

Let w grams of the solute of molecular mass M be present in W grams of the solvent

Molality = 
$$\frac{w/M}{W/1000}$$
 =  $\frac{w}{M \times W} \times 1000$ 

If the density of the solution is known, then molality can be converted into molarity and *vice-versa*.

**4. Mole fraction:** This method is used when the solution is constituted by the use of two or more components. The mole fraction of a substance is defined as the number of moles of the substance divided by the total number of moles of the solution. Taking three components A, B and C,

Components	$\boldsymbol{A}$	В	C
Mass (grams)	$w_1$	$w_2$	$w_3$
Molecular mass	$m_1$	$m_2$	<i>m</i> <sub>3</sub>
No. of gram moles	$\frac{w_1}{m_1}$	$\frac{w_2}{m_2}$	$\frac{w_3}{m_3}$

Total number of gram moles 
$$=\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}$$

Mole fraction of  $A$ ,  $(f_1) = \frac{\frac{w_1}{m_1}}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}}$ 

Mole fraction of  $B$ ,  $(f_2) = \frac{\frac{w_2}{m_2}}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}}$ 

Mole fraction of C, 
$$(f_3) = \frac{\frac{w_3}{m_3}}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}}$$

The sum of mole fraction of a solution is equal to 1, i.e.,

$$f_1 + f_2 + f_3 = 1$$

5. Normality: It is defined as the number of gram equivalents of the solute present in one litre of the solution.

Normality =  $\frac{\text{Number of gram equivalents of the solute}}{\text{Number of litres of the solution}}$ 

or Normality =  $\frac{\text{Number of mg equivalents of the solute}}{\text{Number of mL of the solution}}$ 

or Normality × Number of litres of solution

= Number of gram equivalents of the solute

Let w grams of the solute having equivalent mass E be present in V litres of the solution.

Normality = 
$$\frac{w/E}{V} = \frac{w}{E \times V}$$
  
Normality  $\times E = \frac{w}{V}$ 

or Normality  $\times E = \frac{\pi}{V}$ 

Normality × Equivalent mass of the solute = Strength of the solution (g/L)

Solutions are expressed as 1 N, 2 N, 0.5 N, 0.1 N, 0.01 N,

0.001 N, etc. 1N = Normal = One gram equivalent of the solute per

litre of solution 0.5N = Semi-normal = Half gram equivalent of the solute

per litre of solution 0.1N = Deci-normal = 1/10 gram equivalent of the solute

per litre of solution 0.01N = Centi-normal = 1/100 gram equivalent of the

solute per litre of solution

0.001N = Milli-normal = 1/1000 gram equivalent of the solute per litre of solution

**Normality equation:** Let there be two solutions of substances A and B and  $V_1$  mL of solution A be chemically equivalent to  $V_2$  mL of solution B. Let the equivalent mass of A and B be  $E_1$  and  $E_2$  respectively. Let the normalities and strengths (g/L) of these solutions be  $N_1$ ,  $S_1$  and  $N_2$ ,  $S_2$  respectively.

 $V_1$  mL of the solution will contain substance A

$$=\frac{S_1}{1000}\times V_1\,\mathrm{g}$$

 $V_1$  mL of the solution will contain number of g equivalents of substance A

$$=\frac{S_1\times V_1}{1000\times E_1}$$

Similarly,  $V_2$  mL of the solution will contain number of g equivalents of substance B

$$=\frac{S_2 \times V_2}{1000 \times E_2}$$

At equivalence point, these two will be equal,

So, 
$$\frac{S_1 \times V_1}{1000 \times E_1} = \frac{S_2 \times V_2}{1000 \times E_2}$$
or 
$$\frac{S_1}{E_1} \times V_1 = \frac{S_2}{E_2} \times V_2$$

We know that  $\frac{\text{Strength}}{\text{Equivalent mass}} = \text{Normality}$ 

So, 
$$N_1V_1 = N_2V_2$$
 (Normality equation)

Relationship between normality and molarity: We know that.

Strength of the solution (g/L) = Normality × Equivalent mass Similarly,

Strength of the solution (g/L) = Molarity × Molecular mass

So, 
$$\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular mass of the substance}}{\text{Equivalent mass of the substance}} = n$$

or Normality = 
$$n \times$$
 Molarity

In the case of acids, 'n' is basicity of acids while in the case of bases, 'n' is acidity of bases.

Acid	Basicity	Base	Acidity
HC1	1	NaOH	1
HNO <sub>3</sub>	1	КОН	1
$H_2C_2O_4\cdot 2H_2O$	2	Ba(OH) <sub>2</sub>	2
$H_2SO_4$	2	Ca(OH) <sub>2</sub>	2
H <sub>3</sub> PO <sub>4</sub>	3	Al(OH) <sub>3</sub>	3.

### 17.3 TYPES OF TITRATIONS

Titrations can be classified as:

- 1. Acid-base titrations or acidimetry and alkalimetry
- 2. Oxidation-reduction titrations or redox titrations
- 3. Precipitation titrations
- 4. Complexometric titrations.

#### (1) Acid-base Titrations

When the strength of an acid is determined with the help of a standard solution of base, it is known as **acidimetry**. Similarly, when the strength of a base (alkali) is determined with the help of a standard solution of an acid, it is known as **alkalimetry**. Both these titrations involve neutralisation of an acid with an alkali. In these titrations H<sup>+</sup> ions of the acid combine with OH<sup>-</sup> ions of the alkali to form unionised molecules of water.

$$\begin{array}{ccc} & HA + BOH \longrightarrow BA + H_2O \\ & Acid & Alkali & Salt & Water \end{array}$$
 or 
$$\begin{array}{ccc} & H^+ + A^- + B^+ + OH^- \longrightarrow B^+ + A^- + H_2O \\ & & & H^+ + OH^- \longrightarrow H_2O \end{array}$$

The end point in these titrations is determined by the use of organic dyes which are either weak acids or weak bases. These change their colours within a limited range of hydrogen ion concentrations, *i.e.*, pH of the solution. Phenolphthalein is

a suitable indicator in the titrations of strong alkalies (free from carbonate) against strong acids or weak acids. Methyl orange is used as an indicator in the titrations of strong acids against strong and weak alkalies. As no indicator gives correct results in the titrations of weak acids against weak bases, such titrations are performed by some other methods (physical methods).

#### (2) Oxidation-reduction Titrations

The titrations based on oxidation-reduction reactions are called **redox titrations**. The chemical reactions proceed with transfer of electrons (simultaneous loss or gain of electrons) among the reacting ions in aqueous solutions. Sometimes these titrations are named after the reagent used, as:

(i) Permanganate titrations: These are titrations in which potassium permanganate is used as an oxidising agent in acidic medium. The medium is maintained by the use of dilute sulphuric acid. Potassium permanganate acts as a self-indicator. The potential equation, when potassium permanganate acts as an oxidising agent, is:

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
  
or  $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$ 

Before the end point, the solution remains colourless (when KMnO<sub>4</sub> solution is taken in burette) but after the equivalence point one extra drop of KMnO<sub>4</sub> solution imparts pink colour, *i.e.*, appearance of pink colour indicates the end point. Potassium permanganate is used for the estimation of ferrous salts, oxalic acid, oxalates, hydrogen peroxide, etc. The solution of potassium permanganate is always first standardised before its use.

(ii) Dichromate titrations: These are titrations in which, potassium dichromate is used as an oxidising agent in acidic medium. The medium is maintained acidic by the use of dilute sulphuric acid. The potential equation is:

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$
  
or  $Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr_3^{3+} + 7H_2O$ 

The solution of potassium dichromate can be directly used for titrations. It is mainly used for the estimation of ferrous salts and iodides. In the titration of  $K_2Cr_2O_7$  versus ferrous salt either an external indicator (potassium ferricyanide) or an internal indicator (diphenyl amine) can be used.

(iii) Iodimetric and iodometric titrations: The reduction of free iodine to iodide ions and oxidation of iodide ions to free iodine occurs in these titrations.

$$I_2 + 2e \longrightarrow 2I^-$$
 (reduction)  
 $2I^- \longrightarrow I_2 + 2e$  (oxidation)

These are divided into two types:

(a) Iodimetric titrations: These are the titrations in which free iodine is used. As it is difficult to prepare the solution of iodine (volatile and less soluble in water), it is dissolved in potassium iodide solution.

$$KI + I_2 \longrightarrow KI_3$$
Potassium tri-iodide

This solution is first standardised before use. With the standard solution of  $I_2$ , substances such as sulphite, thiosulphate, arsenite, etc., are estimated.

(b) Iodometric titrations: In iodometric titrations, an oxidising agent is allowed to react in neutral medium or in acidic medium, with excess of potassium iodide to liberate free iodine.

$$KI + Oxidising agent \longrightarrow I_2$$

Free iodine is titrated against a standard reducing agent usually with sodium thiosulphate. Halogens, oxyhalogens, dichromates, cupric ion, peroxides, etc., can be estimated by this method.

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$$

In iodimetric and iodometric titrations, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point the blue or violet colour disappears when iodine is completely changed to iodide.

#### (3) Precipitation Titrations

The titrations which are based on the formation of insoluble precipitates, when the solutions of two reacting substances are brought in contact with each other, are called **precipitation titrations.** For example, when a solution of silver nitrate is added to a solution of sodium chloride or a solution of ammonium thiocyanate, a white precipitate of silver chloride or silver thiocyanate is formed.

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$
  
 $AgNO_3 + NH_4CNS \longrightarrow AgCNS + NH_4NO_3$ 

Such titrations involving silver nitrate are called **argento**metric titrations.

#### (4) Complexometric Titrations

A titration, in which an undissociated complex is formed at the equivalence point, is called **complexometric titration**. These titrations are superior to precipitation titrations as there is no error due to co-precipitation.

$$Hg^{2+} + 2SCN^{-} \longrightarrow Hg(SCN)_{2}$$
  
 $Ag^{+} + 2CN^{-} \longrightarrow [Ag(CN)_{2}]^{-}$ 

EDTA (ethylenediaminetetraacetic acid) is a useful reagent which forms complexes with metals. In the form of disodium salt, it is used to estimate Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in presence of erichrome black-T as an indicator.

# 17.4 DETERMINATION OF EQUIVALENT MASS

Equivalent mass is defined as the number of parts by mass, a chemical species combined with or displaced by 1.008 parts of hydrogen, 8 parts of oxygen or 35.5 parts of chlorine. Equivalent mass is not a constant number. It may change from reaction to reaction especially in the case of redox reactions.

(i) Equivalent mass of an acid: Equivalent mass of an acid is defined as the number of parts by mass of it which contains 1.008 parts by mass of replaceable hydrogen or it is the quantity of the acid by mass that supplies one mole of H<sup>+</sup> ions.

Eq. mass of acid = 
$$\frac{\text{Molecular mass of the acid}}{\text{Number of replaceable H atoms}}$$
  
=  $\frac{\text{Molecular mass of the acid}}{\text{Basicity of the acid}}$ 

Basicity of an acid is equal to number of replaceable hydrogen atoms present in one molecule of the acid.

Acid	Basicity	Mol. mass	Eq. mass
HCl	1	36.5	$\frac{36.5}{1}$ = 36.5
HNO <sub>3</sub>	1	63	$\frac{63}{1} = 63.0$
H <sub>2</sub> SO <sub>4</sub>	2	98	$\frac{98}{2} = 49.0$
СН₃СООН	. 1	60	$\frac{60}{1} = 60.0$
$H_2C_2O_4 \cdot 2H_2O$	2	126	$\frac{126}{2} = 63.0$
$H_3PO_4$	3	98	$\frac{98}{3} = 32.7$
$H_3PO_3$	2	82	$\frac{82}{2} = 41.0$
H <sub>3</sub> PO <sub>2</sub>	1	66	$\frac{66}{1} = 66.0$

(ii) Equivalent mass of a base: Equivalent mass of a base is the quantity of the base by mass that completely reacts with one gram equivalent of an acid. For example,

CaO + 2HCl 
$$\longrightarrow$$
 CaCl<sub>2</sub> + H<sub>2</sub>O  
56 2 × 36.5  
2 g equivalent

Hence, equivalent mass of CaO =  $\frac{56}{2}$  = 28.0

Eq. mass of a base =  $\frac{\text{Molecular mass of the base}}{\text{Acidity of the base}}$ 

Acidity of an alkali is the number of replaceable OHT ions present in one molecule of the base.

Alkali	Acidity	Mol. mass	Eq. mass
NaOH	. 1	40	$\frac{40}{1} = 40$
КОН	1 .	56	$\frac{56}{1}$ = 56
Ca(OH) <sub>2</sub>	2	74	$\frac{74}{2} = 37$
NH <sub>4</sub> OH	1	35	$\frac{35}{1}$ = 35

(iii) Equivalent mass of a salt: It is defined as that mass of the salt which reacts with one gram equivalent of an acid or a base or some other salt. For example,

(a) 
$$Na_2CO_3$$
 +  $2HC1 \longrightarrow 2NaC1 + CO_2 + H_2O$   
1 mole 2 g equivalent

Eq. mass of sodium carbonate =  $\frac{\text{Mol. mass of Na}_2\text{CO}_3}{2}$ 

(b) 
$$\underset{1 \text{ mole}}{\text{AgNO}_3} + \underset{1 \text{ g equivalent}}{\text{HCl}} \rightarrow \underset{1 \text{ AgCl}}{\text{AgCl}} + \underset{1 \text{ HNO}_3}{\text{HNO}_3}$$

Eq. mass of AgNO<sub>3</sub> = 
$$\frac{\text{Mol. mass of AgNO}_3}{1}$$

(c) 
$$NH_4Cl$$
 +  $NaOH \longrightarrow NH_3 + NaCl + H_2O$   
1 mole 1 g equivalent

Eq. mass of 
$$NH_4Cl = \frac{Mol. \text{ mass of } NH_4Cl}{1}$$

$$\begin{array}{cccc} (d) & BaCl_2 & + & Na_2CO_3 \longrightarrow BaCO_3 + 2NaCl \\ \hline & 1 & mole & 2 & g & equivalent \\ \end{array}$$

Eq. mass of BaCl<sub>2</sub> = 
$$\frac{\text{Mol. mass of BaCl}_2}{2}$$

Alternatively, Eq. mass of the salt

= Mol. mass of the salt

Total no. of positive or negative valencies of the radicals

Eq. mass of 
$$CaCO_3 = \frac{100}{2} = 50$$

(iv) Equivalent mass of an oxidising agent:

(a) Available oxygen concept: It is the mass of an oxidising agent which provides 8 grams of oxygen for oxidation. For example,

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$
  
294.2 g 3 × 16  
= 48 g

Eq. mass of 
$$K_2Cr_2O_7 = \frac{294.2}{48} \times 8 = \frac{294.2}{6} = 49.04$$

Potassium permanganate acts as an oxidising agent in acidic, alkaline and neutral mediums.

#### Acidic medium:

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
 $5 \times 16$ 
 $= 80 \text{ g}$ 

Eq. mass of KMnO<sub>4</sub> = 
$$\frac{2 \times 158 \times 8}{80} = \frac{158}{5} = 31.6$$

#### Alkaline medium:

$$2KMnO_4 + 2KOH \longrightarrow K_2MnO_4 + 3H_2O + [O]$$

$$2 \times 158 \text{ g}$$

$$2 \times 8 = 16 \text{ g}$$

Eq. mass of KMnO<sub>4</sub> = 
$$\frac{2 \times 158}{16} \times 8 = 158$$

#### Neutral medium:

$$2KMnO4 + H2O \longrightarrow 2MnO2 + 2KOH + 3[O]$$

$$2 \times 158 g$$

$$3 \times 16 = 48$$

Eq. mass of KMnO<sub>4</sub> = 
$$\frac{2 \times 158}{48} \times 8 = \frac{158}{3} = 52.67$$

(b) Electron concept: The equivalent mass of an oxidising agent is the molecular mass of the oxidising agent divided by the number of electrons gained by one mole of the oxidising agent:

Eq. mass of an oxidising agent

$$= \frac{\text{Molecular mass}}{\text{No. of electrons gained by 1 mole}}$$

#### **Examples:**

(i) Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>:

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$$
  
Eq. mass of  $K_2Cr_2O_7 = \frac{\text{Molecular mass}}{6}$   
 $= \frac{294.2}{6} = 49.03$ 

(ii) Acidified KMnO<sub>4</sub>:

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$
Eq. mass of KMnO<sub>4</sub> = 
$$\frac{Molecular mass}{5}$$
= 
$$\frac{158}{5} = 31.6$$

(iii) Alkaline KMnO<sub>4</sub>:

$$MnO_4 + e \longrightarrow MnO_4^{2-}$$

Eq. mass = Mol. mass = 158.0

(iv) Neutral KMnO<sub>4</sub>:

$$MnO_4^- + 2H_2O + 3e \longrightarrow MnO_2 + 4OH^-$$

Eq. mass of KMnO<sub>4</sub> = 
$$\frac{\text{Mol. mass}}{3} = \frac{158}{3} = 52.67$$

(c) Oxidation number concept: According to this concept,

Equivalent mass =  $\frac{\text{Molecular mass}}{\text{Total change in oxidation number}}$ 

#### **Examples:**

(i) Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is reduced to chromic sulphate in presence of dilute sulphuric acid.

Total change in O.N. = (12 - 6) = 6

Eq. mass of 
$$K_2Cr_2O_7 = \frac{Mol. \text{ mass}}{6} = \frac{294.2}{6} = 49.03$$

(ii) KMnO<sub>4</sub> (acidic medium), KMnO<sub>4</sub>  $\longrightarrow$  MnSO<sub>4</sub> Change in O.N. = (7 - 2) = 5Eq. mass =  $\frac{\text{Mol. mass}}{5} = \frac{158}{5} = 31.6$ 

(iii) KMnO<sub>4</sub> (alkaline medium), KMnO<sub>4</sub> 
$$\longrightarrow$$
 K<sub>2</sub>MnO<sub>4</sub> Change in O.N. =  $(7 - 6) = 1$  Eq. mass = Mol. mass = 158

- (iv) KMnO<sub>4</sub> (neutral medium), KMnO<sub>4</sub>  $\longrightarrow$   $\stackrel{+4}{\text{MnO}_2}$ Change in O.N. = (7 - 4) = 3Eq. mass =  $\frac{\text{Mol. mass}}{3} = \frac{158}{3} = 52.67$
- (v) Equivalent mass of a reducing agent:
- (a) Available oxygen method: The amount of reducing agent which combines with 8 g of oxygen is called its equivalent mass.

Examples: (i) Acidified ferrous ammonium sulphate:

$$\begin{array}{c} 2[FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O] \ + \ H_2SO_4 \ + \ O \longrightarrow Fe_2(SO_4)_3 \\ 2 \ mol. \ mass \\ + \ 2(NH_4)_2SO_4 \ + \ 13H_2O \end{array}$$

Eq. mass of ferrous ammonium sulphate

$$= \frac{2 \text{ Mol. mass}}{16} \times 8$$

$$= \text{Mol. mass} = 392.0$$
(COOH

(ii) Oxalic acid:  $\begin{pmatrix} COOH \\ | & \cdot 2H_2O \\ COOH \end{pmatrix}$ COOH  $\begin{pmatrix} 2H_2O + O \longrightarrow 2CO_2 + 3H_2O \\ COOH & 16 g \end{pmatrix}$ mol. mass

Eq. mass of oxalic acid = 
$$\frac{\text{Mol. mass}}{16} \times 8 = \frac{126 \times 8}{16} = 63.0$$

(b) Electron concept: Equivalent mass of a reducing agent is equal to molecular mass divided by the number of electrons lost by one mole of the substance during its oxidation.

Examples: (i) Acidified ferrous ammonium sulphate:

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$
  
Eq. mass = Mol. mass

(ii) Oxalic acid:

$$C_2O_4^2 \longrightarrow 2CO_2 + 2e$$
  
Eq. mass =  $\frac{\text{Mol. mass}}{2} = \frac{126}{2} = 63.0$ 

(c) Oxidation number concept: According to this concept,

Equivalent mass of reducing agent

Molecular mass

= Total change in O.N. of the oxidised element per molecule

Examples: (i) Ferrous 'ammonium sulphate:

$$\begin{array}{ccc}
+2 & & +3 \\
2\text{FeSO}_4 & \longrightarrow & \text{Fe}_2(\text{SO}_4)_3
\end{array}$$

Change in O.N. per Fe atom = (3 - 2) = 1

Eq. mass = Mol. mass

(ii) Oxalic acid:

H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> 
$$\longrightarrow$$
 2CO<sub>2</sub>
O.N. per C atom; O.N. per C atom = +4

Total change in O.N. =  $(8-6) = 2$ 

Eq. mass =  $\frac{\text{Mol. mass}}{2} = \frac{126}{2} = 63.0$ 

# 17.5 CALCULATIONS OF VOLUMETRIC ANALYSIS

The following points should be kept in mind while making calculations of volumetric exercises.

(i) 1 g equivalent mass of a substance reacts completely with 1 g equivalent mass of any other substance. 1 g equivalent mass of a substance means equivalent mass of the substance in grams. For example,

1 g equivalent mass of NaOH = 40 g of NaOH 1 g equivalent mass of  $H_2SO_4 = 49$  g of  $H_2SO_4$ 1 g equivalent mass of KMnO<sub>4</sub> in acidic medium

= 31.6 g of  $KMnO_4$ 

1 g equivalent mass of hydrated oxalic acid

= 63 g of hydrated oxalic acid

Note: Equivalent mass is a variable quantity and depends on the reaction in which the substance takes part. The nature of the reaction should be known before writing the gram equivalent mass of the substance. For example, in the reactions:

$$2NaCl + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 2HCl$$
 ...(i)

$$2\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$$
 ...(ii)

The value of g equivalent mass of H<sub>2</sub>SO<sub>4</sub> in reaction (i) is 98 g and in reaction (ii) 49 g.

(ii) Number of g equivalents

 $= \frac{\text{Mass of the substance in gram}}{\text{Equivalent mass of the substance}}$ 

Number of g moles =  $\frac{\text{Mass of the substance in gram}}{\text{Molecular mass of the substance}}$ 

=  $\frac{\text{Volume in litres of the substance at N.T.P.}}{22.4}$ 

(only for gases)

Number of milli-equivalents =  $\frac{\text{Mass in gram} \times 1000}{\text{Equivalent mass}}$ 

Number of milli-moles =  $\frac{\text{Mass in gram} \times 1000}{\text{Molecular mass}}$ 

(iii) Molarity = 
$$\frac{\text{No. of moles of the solute}}{\text{No. of litres of the solution}} = \frac{w}{m \times V}$$

Molarity  $\times$  molecular mass = Strength of the solution (g/L)

No. of moles of the solute = Molarity  $\times$  No. of litres of solution

Mass of the solute in  $g(w) = Molarity \times No.$  of litres of solution  $\times Mol.$  mass of solute

Normality = 
$$\frac{\text{No. of g equivalents of the solute}}{\text{No. of litres of the solution}} = \frac{w}{E \times V}$$

Normality × Equivalent mass = Strength of the solution (g/L) No. of equivalents of the solute =

Normality  $\times$  No. of litres of solution Mass of the solute in g (w) = Normality  $\times$  No. of litres of solution  $\times$  Eq. mass of the solute

$$\frac{\text{Molecular mass}}{\text{Equivalent mass}} = n = \frac{\text{Normality}}{\text{Molarity}}$$

Normality =  $n \times Molarity$ 

(iv) Normality equation: When solutions A and B react completely.

$$N_A V_A = N_B V_B$$

Normality of  $A \times$  volume of A = Normality of  $B \times$  volume of B

or 
$$\frac{\text{Strength } A}{\text{Eq. mass } A} \times V_A = \frac{\text{Strength } B}{\text{Eq. mass } B} \times V_B$$

(v) When the solution is diluted, the following formulae can be applied:

or 
$$N_1V_1 = N_2V_2$$
  
or  $M_1V_1 = M_2V_2$   
or  $S_1V_1 = S_2V_2$ 

Before dilution = After dilution

(vi) If a number of acids are mixed, the combined normality of the mixture,  $N_x$  is given:

$$N_x V_x = N_1 V_1 + N_2 V_2 + N_3 V_3 + \dots$$

where  $V_x$  is the total volume of the mixture,  $N_1$  and  $V_1$  are the normality and volume respectively of one acid,  $N_2$  and  $V_2$  of the second acid, and so on.

#### SOME WORKED EXAMPLES

**Example 1.** What is the equivalent mass of:

- (a)  $H_3PO_4$  when neutralized to  $HPO_4^{2-}$
- (b) HClO<sub>4</sub>
- (c) NaIO<sub>3</sub> when reduced to  $I^-$
- (d) NaIO<sub>3</sub> when reduced to  $I_2$
- (e)  $Al(OH)_3$ .

#### Solution:

(a) Molecular mass of  $H_3PO_4 = (3 + 31 + 64) = 98$  g.  $H_3PO_4$  when neutralised to  $HPO_4^{2-}$ , two  $H^+$  ions have been replaced.

Thus, Eq. mass = 
$$\frac{\text{Mol. mass}}{\text{No. of replaceable hydrogen atoms}}$$
  
=  $\frac{98}{2}$  = 49.0 g

(b) HClO<sub>4</sub> molecule contains one replaceable hydrogen atom.

Thus, Eq. mass = 
$$\frac{\text{Mol. mass}}{1} = \frac{100.5}{1} = 100.5$$

(c) 
$$NaIO_3 \longrightarrow I^-$$
Oxidation no. +5 -1

Change in oxidation number = 6

Mol. mass of 
$$NaIO_3 = (23 + 127 + 48) = 198 g$$

Eq. mass of NaIO<sub>3</sub> = 
$$\frac{\text{Mol. mass}}{\text{Change in O.N.}} = \frac{198}{6} = 33.0$$

(d) 
$$NaIO_3 \longrightarrow I_2$$
Oxidation no. +5 0

Change in oxidation no. = 5

Eq. mass of NaIO<sub>3</sub> = 
$$\frac{198}{5}$$
 = 39.6

(e) The acidity of  $Al(OH)_3$  is 3.

Eq. mass of Al(OH)<sub>3</sub> = 
$$\frac{\text{Mol. mass}}{\text{Acidity}} = \frac{78}{3} = 26.0 \text{ g}$$

**Example 2.** Calculate the amount of  $KMnO_4$  present in 200 mL 0.1 N solution in acidic medium (Eq. mass  $KMnO_4 = 31.6$ ).

Solution: Strength of the given solution

= Normality 
$$\times$$
 Eq. mass  
=  $0.1 \times 31.6 = 3.16$  g/L

Amount of KMnO<sub>4</sub> in 200 mL =  $\frac{3.16}{1000}$  × 200 = 0.632 g

**Example 3.** 0.4 g of sodium hydroxide is present in 100 mL of the solution. What is its normality?

#### **Solution:**

Strength of the solution = 
$$\frac{0.4}{100} \times 1000$$
  
= 4.0 g/L  
We know that, Normality =  $\frac{\text{Strength}}{\text{Eq. mass}}$   
Eq. mass of NaOH = 40  
Normality =  $\frac{4}{40} = \frac{1}{10} = 0.1 \text{ N}$ 

Example 4. Determine the number of g equivalents of solute in (a) 100 mL of 5 N HCl (b) 250 mL of 0.1 N  $Na_2CO_3$ .

#### **Solution:**

We know that

Number of g equivalents = Normality  $\times$  Vol. of solution (litres)

- (a) Number of g equivalents of HCl =  $5 \times \frac{100}{1000} = 0.5$
- (b) Number of g equivalents of Na<sub>2</sub>CO<sub>3</sub>

$$=0.1 \times \frac{250}{1000} = 0.025$$

Example 5. Calculate the number of grams of solute in

- (a) 250 mL N/10 HCl
- (b) 500 mL N/20  $Na_2CO_3$  solution.

#### Solution:

(a) No. of g equivalents of HCl =  $\frac{1}{10} \times \frac{250}{1000} = \frac{1}{40}$ 

Mass of HCl = No. of g equivalents × Eq. mass =  $\frac{1}{40}$  × 36.5 = 0.9125 g

(b) No. of g equivalents of Na<sub>2</sub>CO<sub>3</sub> =  $\frac{1}{20} \times \frac{500}{1000} = \frac{1}{40}$ Mass of Na<sub>2</sub>CO<sub>3</sub> = No. of g equivalents × Eq. mass  $= \frac{1}{40} \times 53 = 1.33$  g **Example 6.** What volume of HCl of 2 N HCl be taken to form 500 mL N/10 solution of HCl?

#### **Solution:**

Let  $V_1$  volume of 2 N HCl be taken. Applying the formula,

$$N_1 \ V_1 = N_2 \ V_2$$
  
(Before dilution) (After dilution)  
 $N_1 = 2 \ N, \ V_1 = ?, \ N_2 = N/10$  and  $V_2 = 500 \ \text{mL}$   
So,  $2 \times V_1 = \frac{1}{10} \times 500$   
 $V_1 = \frac{500}{10 \times 2} = 25 \ \text{mL}$ 

i.e., 25 mL 2 N HCl is diluted by addition of 475 mL water to get 500 mL N/10 HCl solution.

**Example 7.** What volumes of 12 N HCl and 3 N HCl must be mixed to form one litre 6 N HCl?

#### Solution:

Let x mL of 12 N HCl and y mL of 3 N HCl be mixed to form one litre 6 N HCl.

So, 
$$x + y = 1000$$
 ...(i)  
Applying the formula  $N_1V_1 + N_2V_2 = N_3V_3$ ,  
 $N_1 = 12 \ N, \ V_1 = x, \ N_2 = 3 \ N, \ V_2 = y, \ N_3 = 6 \ N, \ V_3 = 1000$   
So,  $12x + 3y = 6 \times 1000$  ...(ii)

Putting the value of y = (1000 - x) from eq. (i) in eq. (ii), 12x + 3(1000 - x) = 6000

or 
$$12x - 3x + 3000 = 6000$$
  
or  $9x = 3000$ 

$$x = \frac{3000}{9} = 333.3 \text{ mL}$$

So, y = (1000 - x) = (1000 - 333.3) = 666.7 mLi.e., 333.3 mL 12 N HCl and 666.7 mL 3 N HCl are mixed.

**Example 8.** (a) What is the normality of a 96 per cent solution of  $H_2SO_4$  of specific gravity 1.84?

- (b) How many mL of 96 per cent sulphuric acid solution is necessary to prepare one litre  $0.1 N H_2SO_4$ ?
- (c) To what volume should 10 mL of 96 per cent  $H_2SO_4$  be diluted to prepare 2 N solution?

#### Solution:

Mass of 1 litre of 
$$H_2SO_4$$
 solution = Vol. × Density  
=  $1000 \times 1.84$   
=  $1840 \text{ g}$ 

Mass of H<sub>2</sub>SO<sub>4</sub> present in one litre 96% H<sub>2</sub>SO<sub>4</sub> solution

$$= \frac{96}{100} \times 1840$$
$$= 1766.4 \text{ g}$$

Strength of  $H_2SO_4$  solution = 1766.4 g/L

(a) Normality = 
$$\frac{\text{Strength}}{\text{Eq. mass}} = \frac{1766.4}{49}$$
  
= 36.05 N

(b) Let the volume taken be  $V_1$  mL.

Applying 
$$N_1V_1 = N_2V_2$$
  
 $N_1 = 36.05 \ N$ ,  $V_1 = ?$ ,  $N_2 = \frac{N}{10}$ ,  $V_2 = 1000 \ \text{mL}$   
 $36.05 \times V_1 = \frac{1}{10} \times 1000$   
So,  $V_1 = \frac{1000}{36.05 \times 10} = 2.77 \ \text{mL}$ 

i.e., 2.77 mL of H<sub>2</sub>SO<sub>4</sub> is diluted to one litre.

(c) 
$$N_B V_B = N_A V_A$$
Before dilution After dilution
$$10 \times 36.05 = V_A \times 2$$

$$V_A = 180.25 \text{ mL}$$

i.e., 10 mL of given H<sub>2</sub>SO<sub>4</sub> is diluted to 180.25 mL.

**Example 9.** What is the strength in g per litre of a solution of sulphuric acid-12 mL of which neutralise 15 mL of N/10 sodium hydroxide solution?

#### Solution:

Applying

ying 
$$N_1V_1 = N_2V_2$$
  
(NaOH)  $(H_2SO_4)$   
 $\frac{1}{10} \times 15 = N_2 \times 12$   
 $N_2 = \frac{15}{10 \times 12} = 0.125$   
Normality × Eq. mass = Strength (g/L)  
Strength =  $0.125 \times 49 = 6.125$  g/L

Example 10. 4.9 g of  $H_2SO_4$  is present in 100 mL of the solution. What is the molarity of the solution? Calculate its normality also.

#### Solution:

Solution:  
Strength (g/L) of 
$$H_2SO_4 = \frac{4.9}{100} \times 1000 = 49$$
  
Molarity =  $\frac{\text{Strength}}{\text{Mol. mass}} = \frac{49}{98} = 0.5 \text{ M}$   
Normality =  $n \times \text{Molarity}$   
 $n = \frac{\text{Mol. mass}}{\text{Eq. mass}} = \frac{98}{49} = 2$   
Normality =  $2 \times 0.5 = 1.0$ 

Hence, the  $H_2SO_4$  solution is 1 N.

**Example 11.** 25 mL of  $\frac{N}{10}$  caustic soda solution exactly neutralizes 20 mL of an acid solution containing 7.875 g of acid per litre. Calculate the equivalent mass of the acid.

#### Solution:

$$N_1V_1 = N_2V_2$$
(NaOH) (Acid)
$$\frac{1}{10} \times 25 = N_2 \times 20$$

$$N_2 = \frac{25}{10 \times 20} = 0.125$$

Strength = Normality  $\times$  Eq. mass

Eq. mass of the acid = 
$$\frac{7.875}{0.125}$$
  
= 63.00

Example 12. 150 mL of  $\frac{N}{10}$  HCl is required to react completely with 1.0 g of a sample of limestone. Calculate the percentage purity of calcium carbonate.

#### Solution:

150 mL 
$$\frac{N}{10}$$
 HCl = 150 mL  $\frac{N}{10}$  CaCO<sub>3</sub>  
CaCO<sub>3</sub> + 2HCl  $\longrightarrow$  CaCl<sub>2</sub> + H<sub>2</sub>O + CO<sub>2</sub>  
Mol. mass 2g Eq.

Eq. mass of 
$$CaCO_3 = \frac{40 + 12 + 48}{2} = \frac{100}{2} = 50$$

Mass of CaCO<sub>2</sub> present in 150 mL N/10 solution

$$= 50 \times \frac{1}{10} \times \frac{150}{1000} = 0.75 \text{ g} \left[ N \times E \times \frac{V}{1000} \right]$$
Purity =  $\frac{0.75}{1} \times 100 = 75\%$ 

Example 13. 0.63 g of dibasic acid was dissolved in water. The volume of the solution was made 100 mL, 20 mL of this acid solution required 10 mL  $\frac{N}{5}$  NaOH solution. What is the equivalent mass and molecular mass of the acid?

#### **Solution:**

$$N_1V_1 \equiv N_2V_2$$
(Acid) (NaOH)
$$N_1 \times 20 = \frac{1}{5} \times 10$$

$$N_1 = \frac{1}{5} \times \frac{10}{20} = \frac{1}{10}$$

Strength of the acid solution = Eq. mass of the acid × Normality

$$= E \times \frac{1}{10} = \frac{E}{10} \text{ g/L}$$

Mass of acid in 100 mL of the solution  $=\frac{E}{10} \times \frac{100}{1000} = \frac{E}{100}$ Mass of acid in 100 mL of the solution = 0.63 g (given)

So, 
$$\frac{E}{100} = 0.63$$
 or  $E = 60$   
Mol. mass = Basicity × Eq. mass  
 $= 2 \times 63 = 126$ 

Example 14. 10.875 g of a mixture of NaCl and Na<sub>2</sub>CO<sub>3</sub> was dissolved in water and the volume made upto 250 mL, 20 mL of this solution required 75.5 mL of  $\frac{N}{10}$  H<sub>2</sub>SO<sub>4</sub>. Find out the percentage composition of the mixture.

#### Solution:

Only Na<sub>2</sub>CO<sub>3</sub> will react with H<sub>2</sub>SO<sub>4</sub>.  
Applying 
$$N_1V_1 \equiv N_2V_2$$
  
(Na<sub>2</sub>CO<sub>3</sub>) (H<sub>2</sub>SO<sub>4</sub>)

$$N_1 \times 20 = 75.5 \times \frac{1}{10}$$

$$N_1 = \frac{75.5}{20 \times 10} = 0.3775$$

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
1 mol. mass 2 g eq.

Eq. mass of Na\_2CO\_3 =  $\frac{106}{2}$  = 53

Mass of Na<sub>2</sub>CO<sub>3</sub> present in 250 mL 0.3775 N solution
$$= \frac{N \times E \times V}{1000} = \frac{0.3775 \times 53 \times 250}{1000}$$

$$= 5.0018 \text{ g}$$
Mass of NaCl =  $(10.875 - 5.0018) = 5.8732 \text{ g}$ 

$$\text{Na2CO}_3 = \frac{5.0018}{10.875} \times 100 = 45.99\%$$

$$\text{NaCl} = \frac{5.8732}{10.875} \times 100 = 54.0\%$$

**Example 15.** A quantity of ammonium chloride was heated with 100 mL of 0.8 N NaOH solution till the reaction was complete. The excess of NaOH was neutralised with 12.5 mL of  $0.75\ NH_2SO_4$ . Calculate the quantity of ammonium chloride. **Solution :** 

12.5 mL of 0.75 N H<sub>2</sub>SO<sub>4</sub>  $\equiv$  12.5 mL of 0.75 N NaOH 12.5 mL of 0.75 N NaOH  $\equiv$  11.72 mL of 0.8 N NaOH

NaOH solution used by NH<sub>4</sub>Cl

= 
$$(100 - 11.72)$$
 mL of  $0.8 N$  NaOH  
=  $88.28$  mL of  $0.8 N$  NaOH  
=  $88.28$  mL of  $0.8 N$  NH<sub>4</sub>Cl

Mass of NH<sub>4</sub>Cl present in 88.28 mL of 0.8 N NH<sub>4</sub>Cl solution  $= \frac{N \times E \times V}{1000} = \frac{0.8 \times 53.5 \times 88.28}{1000}$  = 3.7783 g

[Eq. mass of 
$$NH_4Cl = 53.5$$
]

**Example 16.** A sample of  $Na_2CO_3 \cdot H_2O$  weighing 0.62 g is added to 100 mL of 0.1 N sulphuric acid. Will the resulting solution be acidic, basic or neutral? [At. mass H = 1, C = 12, O = 16, Na = 23, S = 32]

#### **Solution:**

Mass of  $Na_2CO_3 \cdot H_2O = 0.62$  g

No. of g equivalents = 
$$\frac{\text{Mass}}{\text{Eq. mass}} = \frac{0.62}{62} = 0.01$$

[Eq. mass of Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O = 
$$\frac{124}{2}$$
 = 62]

No. of g equivalents of 
$$H_2SO_4$$
 in 100 mL =  $\frac{0.1}{1000} \times 100$   
=  $\frac{0.1}{10} = 0.01$ 

Both the substances are present in same equivalent; they will completely neutralise each other and, hence, the resulting solution will be neutral.

**Example 17.** 0.1435 g AgCl is obtained from 20 mL HCl. Determine the normality of the acid. [H = 1, Cl = 35.5, Ag = 108]

**Solution:** 

**Solution:** 

$$\begin{array}{ccc} \text{AgNO}_3 + \text{HCl} & \longrightarrow \text{AgCl} + \text{HNO}_3 \\ 170 & 36.5 & 143.5 \\ 1 \text{ g eq.} & 1 \text{ g eq.} & 1 \text{ g eq.} \end{array}$$

Mass of AgCl obtained = 0.1435 g

No. of g equivalents = 
$$\frac{0.1435}{1435}$$
 = 0.001

Thus, 20 mL of HCl will also contain 0.001 g equivalent of HCl.

Normality of HCl = 
$$\frac{0.001}{20} \times 1000$$
  
= 0.05 N

**Example 18.** 40 mL of HCl is exactly neutralised by 20 mL of NaOH solution. The resulting neutral solution is evaporated to dryness and the residue is found to have a mass of 0.117 g. Calculate the normality of the HCl and NaOH.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$
  
36.5 40 58.5  
1 g eq. 1 g eq. 1 g eq.

Mass of NaCl obtained = 0.117 g

Eq. mass of 
$$NaCl = 58.5$$

No. of g equivalents of NaCl = 
$$\frac{0.117}{58.5}$$
 = 0.002

Thus,  $0.002~\rm g$  eq. of HCl will react with  $0.002~\rm g$  eq. of NaOH to form  $0.002~\rm g$  eq. NaCl.

Normality of HCl = 
$$\frac{0.002}{40} \times 1000 = 0.05 \ N$$
  
Normality of NaOH =  $\frac{0.002}{20} \times 1000 = 0.10 \ N$ 

**Example 19.** 1.03 g mixture of sodium carbonate and calcium carbonate require 20 mL N HCl for complete neutralisation. Calculate the percentage of sodium carbonate and calcium carbonate in the given mixture.

#### **Solution:**

$$\begin{array}{c} \text{Na}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \\ 106 & 2 \times 36.5 \\ \text{Eq. mass} & 53 & 36.5 \\ 1 \text{ g eq.} & 1 \text{ g eq.} \\ \text{CaCO}_3 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2 \\ 100 & 2 \times 36.5 \\ \text{Eq. mass} & 50 & 36.5 \\ 1 \text{ g eq.} & 1 \text{ g eq.} \end{array}$$

Let  $x \in CaCO_3$  be present in the mixture.

Mass of Na<sub>2</sub>CO<sub>3</sub> in the mixture = 
$$(1.03 - x)g$$

No. of g equivalents of 
$$CaCO_3 = \frac{x}{50}$$

No. of g equivalents of Na<sub>2</sub>CO<sub>3</sub> = 
$$\frac{(1.03 - x)}{53}$$

No. of g equivalents in 20 mL N HCl = 
$$\frac{\text{Normality} \times \text{Vol.}}{1000}$$
$$= \frac{1 \times 20}{1000} = \frac{1}{50}$$

At equivalence point,

No. of g equivalents of  $CaCO_3 + No.$  of g equivalents of  $Na_2CO_3 = No.$  of gram equivalents of HCl

$$\frac{x}{50} + \frac{1.03 - x}{53} = \frac{1}{50}$$
or
$$x = 0.50$$

$$CaCO_3 = 0.50 \text{ g}, \qquad \% \text{ CaCO}_3 = \frac{0.50}{1.03} \times 100 = 48.54$$

$$Na_2CO_3 = 0.53 \text{ g}, \qquad \% \text{ Na}_2CO_3 = \frac{0.53}{1.03} \times 100 = 51.46$$

**Example 20.** 1.325 g of anhydrous sodium carbonate are dissolved in water and the solution made upto 250 mL. On titration 25 mL of this solution neutralise 20 mL of a solution of sulphuric acid. How much water should be added to 450 mL of this acid solution to make it exactly N/12?

#### **Solution:**

Eq. mass of Na<sub>2</sub>CO<sub>3</sub> = 
$$\frac{\text{Mol.mass}}{2} = \frac{106}{2} = 53$$

250 mL of the sodium carbonate solution contains = 1.325 g 1000 mL of the sodium carbonate solution contains

Normality of Na<sub>2</sub>CO<sub>3</sub> solution = 
$$\frac{1.325 \text{ g}}{250} \times 1000 = 5.300 \text{ g}$$

Normality of Na<sub>2</sub>CO<sub>3</sub> solution =  $\frac{\text{Strength (g/L)}}{\text{Eq. mass}}$ 

$$= \frac{5.30}{53} = \frac{1}{10}N$$

Applying  $N_1V_1 = N_2V_2$ 

$$(Na_2CO_3) \quad (H_2SO_4)$$

$$\frac{1}{10} \times 25 = N_2 \times 20$$

$$N_2 = \frac{25}{10 \times 20} = \frac{1}{8}$$

Applying  $N_BV_B = N_AV_A$ 

$$(\text{Before dilution)} \quad (\text{After dilution})$$

$$\frac{1}{8} \times 450 = \frac{1}{12} \times V_A$$

$$V_A = \frac{450 \times 12}{8} = 675 \text{ mL}$$

Water to be added for dilution = (675 - 450) = 225 mL

**Example 21.** A sample of sodium carbonate contains sodium sulphate also. 1.5 g of the sample is dissolved in water and volume raised to 250 mL. 25 mL of this solution requires  $20 \text{ mL of } \frac{N}{10} H_2 SO_4$  solution for neutralisation. Calculate the percentage of sodium carbonate in the sample.

#### **Solution:**

Only Na<sub>2</sub>CO<sub>3</sub> will react with H<sub>2</sub>SO<sub>4</sub>.

Applying 
$$N_1V_1 = N_2V_2$$
 $(Na_2CO_3) = (H_2SO_4)$ 
 $N_1 \times 25 = 20 \times \frac{1}{10}$ 
 $N_1 = \frac{20}{25 \times 10} = 0.08$ 

Eq. mass of Na<sub>2</sub>CO<sub>3</sub> =  $\frac{\text{Mol. mass}}{2} = \frac{106}{2} = 53$ 

Mass of Na<sub>2</sub>CO<sub>3</sub> present in 250 mL 0.08 N solution

$$=\frac{N\times E\times V}{1000}=\frac{0.08\times 53\times 250}{1000}=1.06 \text{ g}$$

Percentage of Na<sub>2</sub>CO<sub>3</sub> in the mixture =  $\frac{1.06}{1.50} \times 100 = 70.67$ 

**Example 22.** A solution containing 4.2 g of KOH and  $Ca(OH)_2$  is neutralised by an acid. If it consumes 0.1 equivalent of the acid, calculate the composition of the sample.

#### Solution:

Let mass of KOH be present in mixture = a g and Mass of Ca(OH)<sub>2</sub> = (4.2 - a) g

Eq. mass of KOH = 56; Eq. mass of  $Ca(OH)_2 = \frac{74}{2} = 37$ No. of g equivalents of KOH + No. of g equivalents of  $Ca(OH)_2$ = No. of g equivalents of the acid

$$\frac{a}{56} + \frac{(4.2 - a)}{37} = 0.1$$
or
$$37a - 56a = 0.1 \times 56 \times 37 - 4.2 \times 56$$
or
$$19a = 28$$

$$a = \frac{28}{19} = 1.47$$

Mass of KOH in the sample = 1.47 g

Percentage of KOH = 35

and Percentage of  $Ca(OH)_2 = 100 - 35 = 65$ 

**Example 23.** 1.725 g of a metal carbonate is mixed with 300 mL of  $\frac{N}{10}$  HCl. 10 mL of  $\frac{N}{2}$  sodium hydroxide were required to neutralise excess of the acid. Calculate the equivalent mass of the metal carbonate.

#### Solution:

10 mL of 
$$\frac{N}{2}$$
 NaOH solution  
= 10 mL of  $\frac{N}{2}$  HCl solution  
= 50 mL of  $\frac{N}{10}$  HCl solution

Volume of  $\frac{N}{10}$  HCl used for neutralisation = 300 – 50 = 250 mL

250 mL of  $\frac{N}{10}$  HCl = 250 mL of  $\frac{N}{10}$  metal carbonate solution Let the equivalent mass of metal carbonate be E. Mass of metal carbonate present in solution

$$= \frac{N \times E \times V}{1000} = 1.725$$

$$= \frac{1 \times E \times 250}{10 \times 1000} = 1.725$$
$$= \frac{E}{40} = 1.725$$
$$E = 40 \times 1.725 = 69$$

Example 24. 1.575 g of oxalic acid  $(COOH)_2$ · $xH_2O$  are dissolved in water and the volume made upto 250 mL. On titration 16.68 mL of this solution requires 25 mL of  $\frac{N}{15}$  NaOH solution for complete neutralisation. Calculate x.

**Solution:** 

25 mL of 
$$\frac{N}{15}$$
 NaOH solution = 25 mL of  $\frac{N}{15}$  oxalic acid

Mass of oxalic acid present in 25 mL of  $\frac{N}{15}$  oxalic acid solution

$$= \frac{N \times E \times V}{1000} = \frac{1 \times (90 + 18x) \times 25}{15 \times 2 \times 1000}$$
$$= \frac{(90 + 18x)}{1200} g$$

Actually  $\frac{(90+18x)}{1200}$  g oxalic acid is present in 16.68 mL solution.

250 mL of the solution contains oxalic acid

$$= \frac{(90+18x)\times 250}{1200\times 16.68} = 1.575 \text{ (given)}$$
or
$$90+18x = \frac{1.575\times 1200\times 16.68}{250} = 126$$
or
$$18x = 126-90 = 36$$

$$x = 2$$

# 17.6 TO DETERMINE THE AMOUNT OF SODIUM HYDROXIDE AND SODIUM CARBONATE IN A GIVEN MIXTURE

The method involves the use of two indicators, phenolphthalein and methyl orange. When a mixture of sodium hydroxide and sodium carbonate is titrated with a standard solution of hydrochloric acid, using phenolphthalein as indicator, the strong base is neutralised first.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$
 ...(i)

After the completion of above reaction, the carbonate is converted completely to bicarbonate.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$
 ...(ii)

At this point, phenolphthalein changes from pink to colourless marking the first end point. Methyl orange is added now and orange-yellow colour is developed.

On adding acid, the bicarbonate is converted to carbonic acid and colour changes to red marking the second end point.

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2CO_3$$
 ...(iii)

Let  $V_1$  mL of acid be required upto first end point and  $V_2$  mL of acid be required from first end point to second end point.

V <sub>1</sub> mL	NaOH	$(V_1 - V_2) \text{ mL}$ acid
1st end point	$\frac{1}{2}$ Na <sub>2</sub> CO <sub>3</sub>	ì
$V_2$ mL 2nd end point	$\frac{1}{2}$ Na <sub>2</sub> CO <sub>3</sub>	$2V_2 \text{ mL}$ Acid

Suppose, VmL of alkali solution is titrated with hydrochloric acid of normality N. From the above readings, it is possible to calculate the amounts of NaOH and Na<sub>2</sub>CO<sub>3</sub>.

Amount of NaOH in mixture = 
$$40 \times N \times \frac{(V_1 - V_2)}{V}$$
 g/L

Amount of Na<sub>2</sub>CO<sub>3</sub> in mixture = 
$$53 \times N \times \frac{2V_2}{V}$$
 g/L

#### 17.6.19 TO DETERMINE THE AMOUNT OF SODIUM CARBONATE AND BICARBONATE IN A MIXTURE

The method involves the successive use of two indicators, phenolphthalein and methyl orange. When a cold mixture of sodium carbonate and sodium bicarbonate is titrated against a standard solution of hydrochloric acid, using phenolphthalein as indicator, the sodium carbonate is converted into sodium bicarbonate first and colour changes from pink to colourless marking the first end point.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

If methyl orange is added at this stage, solution acquires orange yellow colour. On further addition of the acid, all the bicarbonate is neutralised and the colour changes to red. This is the second end point.

$$NaHCO_3 + HC1 \longrightarrow NaC1 + H_2CO_3$$

Suppose V mL of mixture is titrated with a standard hydrochloric acid of normality N. Let  $V_1$  mL of the acid be required upto first end point and  $V_2$  mL of the acid be required from first end point to second end point.

V <sub>1</sub> mL First end point	$\left\{ \frac{1}{2} \operatorname{Na_2CO_3} \right\}$	$2V_1$ mL
$V_2$ mL Second end point	$\left\{\begin{array}{c} \frac{1}{2} \text{Na}_2 \text{CO}_3 \\ \text{NaHCO}_3 \end{array}\right\}$	$(V_2 - V_1)$ mL

From these readings, it is possible to calculate the amounts of sodium carbonate and sodium bicarbonate.

Amount of Na<sub>2</sub>CO<sub>3</sub> = 
$$53 \times N \times \frac{2V_1}{V}$$
 g/L

Amount of NaHCO<sub>3</sub> = 84 × 
$$N \times \frac{(V_2 - V_1)}{V}$$
 g/L

**Example 25.** 25 mL of a mixture of NaOH and Na<sub>2</sub>CO<sub>3</sub> when titrated with N/10 HCl using phenolphthalein indicator required 25 mL HCl. The same volume of mixture when titrated with N/10 HCl using methyl orange indicator required 30 mL of HCl. Calculate the amount of Na<sub>2</sub>CO<sub>3</sub> and NaOH in one litre of this mixture.

#### **Solution:**

When phenolphthalein is the indicator, whole of NaOH has been neutralised and carbonate converted into bicarbonate, *i.e.*,

$$NaOH + HCl \longrightarrow NaCl + H_2O$$
  
 $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$ 

So, 25 mL  $\frac{N}{10}$  HCl = NaOH + 1/2 Na<sub>2</sub>CO<sub>3</sub> present in 25 mL of mixture

In another titration when methyl orange is the indicator, whole of NaOH has been neutralised and carbonate converted into carbonic acid, *i.e.*,

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2CO_3$$

30 mL  $\frac{N}{10}$  HCl = NaOH + Na<sub>2</sub>CO<sub>3</sub> present in 25 mL of mixture. Hence.

(30-25) mL  $\frac{N}{10}$  HCl  $\equiv \frac{1}{2}$  Na<sub>2</sub>CO<sub>3</sub> present in 25 mL of mixture. Hence,

10 mL 
$$\frac{N}{10}$$
 HCl  $\equiv$  Na<sub>2</sub>CO<sub>3</sub> present in 25 mL of mixture  
 $\equiv$  10 mL  $\frac{N}{10}$  Na<sub>2</sub>CO<sub>3</sub> solution

Amount of Na<sub>2</sub>CO<sub>3</sub> = 
$$\frac{53 \times 10}{10 \times 1000}$$
 = 0.053 g

This amount of Na<sub>2</sub>CO<sub>3</sub> is present in 25 mL of mixture. The amount present in one litre of mixture

$$= \frac{0.053}{25} \times 1000 = 2.12 \text{ g}$$

(30 – 10) mL  $\frac{N}{10}$  HCl ≡ NaOH present in 25 mL mixture ≡ 20 mL  $\frac{N}{10}$  NaOH

Amount of NaOH in 25 mL of mixture =  $\frac{40 \times 20}{10 \times 1000}$  = 0.08 g

The amount present in one litre of mixture =  $\frac{0.08}{25} \times 1000$ = 3.20 g

**Example 26.** 25 mL of a mixture of NaOH + Na<sub>2</sub>CO<sub>3</sub>, when titrated with N/10 HCl using phenolphthalein indicator required 25 mL HCl to decolourise phenolphthalein. At this stage methyl orange was added and addition of acid was continued. The second end point was reached after further addition of 5 mL of the acid. Calculate the amount of Na<sub>2</sub>CO<sub>3</sub> and NaOH in one litre of the solution.

#### **Solution:**

Between first and second end points,

5 mL  $\frac{N}{10}$  HCl =  $\frac{1}{2}$  Na<sub>2</sub>CO<sub>3</sub> present in 25 mL of a mixture

or 10 mL 
$$\frac{N}{10}$$
 HC1 = Na<sub>2</sub>CO<sub>3</sub> present in 25 mL of a mixture  
= 10 mL  $\frac{N}{10}$  Na<sub>2</sub>CO<sub>3</sub> = 0.053 g Na<sub>2</sub>CO<sub>3</sub>

Amount of Na<sub>2</sub>CO<sub>3</sub> in one litre of mixture = 
$$\frac{0.053}{25} \times 1000$$

$$= 2.12 \text{ g}$$

$$(25 - 5) \text{ mL } N/10 \text{ HCl} = \text{NaOH present in } 25 \text{ mL of mixture}$$

$$= 25 \text{ mL } \frac{N}{10} \text{ NaOH} = 0.08 \text{ g NaOH}$$

Amount of NaOH in one litre of mixture = 
$$\frac{0.08}{25} \times 1000$$
  
= 3.2 g

**Example 27.** A solution contains Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>. 10 mL of the solution required 2.5 mL of 0.1 M H<sub>2</sub>SO<sub>4</sub> for neutralisation using phenolphthalein as indicator. Methylorange is then added when a further 2.5 mL of 0.2 M H<sub>2</sub>SO<sub>4</sub> was required. Calculate the amount of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> in one litre of the solution.

#### **Solution:**

2.5 mL of 0.1 
$$M$$
 H<sub>2</sub>SO<sub>4</sub> = 2.5 mL of 0.2  $N$  H<sub>2</sub>SO<sub>4</sub> =  $\frac{1}{2}$  Na<sub>2</sub>CO<sub>3</sub> present in 10 mL of mixture

So,

5 mL of 0.2 N H<sub>2</sub>SO<sub>4</sub> = Na<sub>2</sub>CO<sub>3</sub> present in 10 mL of mixture  

$$\equiv 5 \text{ mL of } 0.2 \text{ N Na2CO3}$$

$$\equiv \frac{0.2 \times 53}{1000} \times 5 = 0.053 \text{ g}$$

Amount of Na<sub>2</sub>CO<sub>3</sub> = 
$$\frac{0.053}{10} \times 1000 = 5.3$$
 g/L of mixture.

Between first and second end points,

= 2.5 mL of 0.2 
$$M$$
 H<sub>2</sub>SO<sub>4</sub> used  
= 2.5 mL of 0.4  $N$  H<sub>2</sub>SO<sub>4</sub> used

= 5 mL of 
$$0.2 N H_2 SO_4$$
 used

$$\equiv \frac{1}{2} \text{ Na}_2\text{CO}_3 + \text{Na}\text{HCO}_3 \text{ present in 10 mL of mixture}$$

$$(5 - 2.5) \text{ mL } 0.2 \text{ N H}_2\text{SO}_4$$

$$\equiv$$
 NaHCO<sub>3</sub> present in 10 mL of mixture  
 $\equiv$  2.5 mL 0.2 N NaHCO<sub>3</sub>  
 $\equiv \frac{0.2 \times 84}{1000} \times 2.5 = 0.042$  g

Amount of NaHCO<sub>3</sub> = 
$$\frac{0.042}{10}$$
 × 1000 = 4.20 g/L of mixture.

#### 17.7 KJELDAHL'S PROCESS

This method is used for the estimation of nitrogen in organic substances. This method is based on the fact that when an organic compound containing nitrogen is heated with concentrated sulphuric acid, the nitrogen in it is converted quantitatively into ammonium sulphate. The resultant liquid is then treated with excess of sodium hydroxide and the liberated ammonia gas is absorbed in excess of standard acid solution. The unreacted acid is estimated by titration with standard alkali. The difference of the two gives the volume of standard acid that actually combined with the evolved ammonia. From this, the percentage of nitrogen in the organic compound can be calculated.

Let the mass of organic substance be w g and V mL of N HCl is required for complete neutralisation of evolved ammonia; then,

$$V \text{ mL } N \text{ HCl} \equiv V \text{ mL } N \text{ NH}_3$$

$$17 \text{ g NH}_3 \equiv 14 \text{ g nitrogen}$$
Amount of nitrogen in  $V \text{ mL } N \text{ NH}_3 = \frac{14 \times N \times V}{1000}$ 

$$\% \text{ of nitrogen} = \frac{14 \times N \times V}{w \times 1000} \times 100$$

$$= \frac{1.4 \times N \times V}{w}$$

where N stands for normality of acid used
V stands for volume of acid used
and w stands for mass of organic substance.

**Example 28.** 1.0 g of an organic compound was analysed by Kjeldahl's process. The ammonia produced was absorbed in 80 mL of  $\frac{N}{5}$  H<sub>2</sub>SO<sub>4</sub>. The excess acid required 34 mL of  $\frac{N}{10}$  NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.

#### **Solution:**

$$34 \text{ mL } \frac{N}{10} \text{ NaOH} \equiv 34 \text{ mL } \frac{N}{10} \text{ H}_2 \text{SO}_4$$
$$\equiv 17 \text{ mL } \frac{N}{5} \text{ H}_2 \text{SO}_4$$

Thus, acid used for neutralisation of  $NH_3 = (80 - 17)$ = 63 mL

So, 63 mL 
$$\frac{N}{5}$$
 H<sub>2</sub>SO<sub>4</sub> = 63 mL  $\frac{N}{5}$  NH<sub>3</sub>

Amount of nitrogen in the given sample =  $\frac{14}{5} \times \frac{63}{1000}$  g

% of nitrogen =  $\frac{14}{5} \times \frac{63}{1000} \times \frac{100}{1}$ 
=  $\frac{1.4 \times 63}{5}$ 

= 17.64

# SOME WORKED EXAMPLES ON OXIDATION-REDUCTION TITRATIONS

**Example 29.** 0.5 g of an oxalate was dissolved in water and the solution made to 100 mL. On titration 10 mL of this solution required 15 mL of  $N/20 \text{ KMnO}_4$ . Calculate, the percentage of oxalate in the sample.

#### **Solution:**

15 mL  $\frac{N}{20}$  KMnO<sub>4</sub> = 10 × Normality of oxalate solution

Normality of oxalate solution =  $\frac{15}{10} \times \frac{1}{20} = \frac{3}{40}$ 

Strength of oxalate solution = Normality  $\times$  Eq. mass of oxalate

= 
$$\frac{3}{40} \times 44 = 3.3$$
 g/L [Eq. mass  $C_2O_4^{2-} = \frac{88}{2} = 44$ ]

Amount of oxalate in 100 mL solution =  $\frac{3.3}{1000} \times 100 = 0.33$  g % of oxalate =  $\frac{0.33}{0.5} \times 100 = 66.0$ 

**Example 30.** How many mL of a 0.05 M  $KMnO_4$  solution are required to oxidise 2.0 g of  $FeSO_4$  in a dilute solution (acidic).

#### **Solution:**

$$10\text{FeSO}_4 + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4$$

$$10 \times 151.8 \quad 2 \times 158 \quad + 5\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}_4$$

 $10 \times 151.8$  g of FeSO<sub>4</sub> require KMnO<sub>4</sub> =  $2 \times 158$  g

2 g of FeSO<sub>4</sub> will require KMnO<sub>4</sub> = 
$$\frac{2 \times 158 \times 2}{10 \times 1518}$$
g

Suppose V mL of KMnO<sub>4</sub> solution (0.05 M) is required.

Amount of KMnO<sub>4</sub> in this solution =  $\frac{158 \times 0.05}{1000} \times V$ 

Thus, 
$$\frac{158 \times 0.05 \times V}{1000} = \frac{2 \times 158 \times 2}{10 \times 151.8}$$
$$V = 52.7 \text{ mL}$$

**Example 31.** 5.5 g of a mixture of  $FeSO_4$ .7 $H_2O$  and  $Fe_2(SO_4)_3$ .9 $H_2O$  required 5.4 mL of 0.1 N KMn $O_4$  solution for complete oxidation. Calculate the gram mole of hydrated ferric sulphate in the mixture.

[At. mass 
$$H = 1$$
,  $O = 16$ ,  $S = 32$ ,  $Fe = 56$ ]

#### **Solution:**

Only FeSO<sub>4</sub>·7H<sub>2</sub>O will be oxidised by KMnO<sub>4</sub>.

Mol. mass of  $FeSO_4 \cdot 7H_2O = 278$ 

As the conversion involves one electron,

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$
,

The Eq. mass of  $FeSO_4.7H_2O = \frac{278}{1} = 278$ 

5.4 mL of 0.1 N KMnO<sub>4</sub>

 $\equiv 5.4 \text{ mL of } 0.1 \text{ N FeSO}_4.7\text{H}_2\text{O} \text{ solution}$ 

Amount of FeSO<sub>4</sub>·7H<sub>2</sub>O = 
$$\frac{0.1 \times 278}{1000} \times 5.4 = 0.15 \text{ g}$$

Amount of  $Fe_2(SO_4)_3.9H_2O = (5.5 - 0.15) = 5.35 g$ Mol. mass of  $Fe_2(SO_4)_3.9H_2O = 562$ 

No. of g moles of 
$$Fe_2(SO_4)_3 \cdot 9H_2O = \frac{Mass}{Mol. mass}$$
  
=  $\frac{5.35}{562} = 0.00952$   
=  $9.52 \times 10^{-3}$ 

**Example 32.** 50 mL of an aqueous solution of  $H_2O_2$  was treated with an excess of KI solution and dilute  $H_2SO_4$ . The liberated iodine required 20 mL 0.1 N  $Na_2S_2O_3$  solution for complete interaction. Calculate the concentration of  $H_2O_2$  in g/L.

#### Solution:

$$\begin{array}{c} \text{H}_2\text{O}_2 + 2\text{KI} + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{I}_2 \\ & 2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \end{array}$$

Eq. mass 
$$H_2O_2 = \frac{34}{2} = 17$$

20 mL 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 20 mL 0.1 N I<sub>2</sub> solution  $\equiv$  20 mL 0.1 N H<sub>2</sub>O<sub>2</sub> solution

Amount of H<sub>2</sub>O<sub>2</sub> in 50 mL aq. solution

$$= \frac{0.1 \times 17}{1000} \times 20 = 0.034 \text{ g}$$

Concentration in g/L = 
$$\frac{0.034}{50}$$
 × 1000 = 0.68

**Example 33.** 0.124 g of iron wire was dissolved in dilute  $H_2SO_4$  in oxygen free atmosphere and the resultant solution was titrated against 0.09672 N solution of KMnO<sub>4</sub>. The titre value was 22.90 mL. Calculate the percentage purity of iron wire.

#### **Solution:**

22.90 mL 0.09672 N KMnO<sub>4</sub>  $\equiv$  22.90 mL 0.09672 N FeSO<sub>4</sub> Amount of FeSO<sub>4</sub> in the solution =  $\frac{0.09672 \times 152 \times 22.90}{1000}$ = 0.3366 g

Amount of iron in 0.3366 g of FeSO<sub>4</sub> =  $\frac{56}{152}$  × 0.3366 = 0.124 g

Thus, percentage = 
$$\frac{0.124}{0.124} \times 100 = 100$$

The iron wire is 100% pure.

**Example 34.** A sample of hydrazine sulphate  $(N_2H_6SO_4)$  was dissolved in 100 mL of water. 10 mL of this solution was reacted with excess of FeCl<sub>3</sub> solution and warmed to complete the reaction. Ferrous ion formed was estimated and it required 20 mL of  $\frac{M}{50}$  KMnO<sub>4</sub>. Estimate the amount of hydrazine sulphate in one litre of solution.

Reactions: 
$$4 Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4Fe^{2+} + 4H^+$$
  
 $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ 

#### **Solution:**

$$20 \text{ mL} \frac{M}{50} \text{ KMnO}_4 = 20 \text{ mL} \frac{N}{10} \text{ KMnO}_4$$

$$\left[ \text{Equivalent mass of KMnO}_4 = \frac{\text{Molecular mass}}{5} \right]$$

$$20 \text{ mL} \frac{N}{10} \text{ KMnO}_4 = 20 \text{ mL} \frac{N}{10} \text{ ferrous ion}$$

$$\equiv 20 \text{ mL} \frac{N}{10} \text{ FeCl}_3$$

$$\equiv 20 \text{ mL} \frac{N}{10} \text{ N}_2 \text{H}_6 \text{SO}_4$$

$$\text{Eq. mass N}_2 \text{H}_6 \text{SO}_4 = \frac{\text{Mol.mass}}{4} = \frac{130}{4} = 32.5$$

[Since change in O.N.  $(N_2H_4 \rightarrow N_2)$  per molecule = 4] Amount of hydrazine sulphate in 10 mL of solution

$$= \frac{1}{10} \times \frac{32.5}{1000} \times 20 = 0.065 \text{ g}$$

Amount of hydrazine sulphate in one litre of solution

$$= \frac{0.065}{10} \times 1000 = 6.50 \text{ g}$$

**Example 35.** 0.1 M KMnO<sub>4</sub> is used for the following titration. What volume of the solution in mL will be required to react with 0.158 g of  $Na_2S_2O_3$ ?

$$S_2O_3^{2-} + MnO_4^- + H_2O \longrightarrow MnO_2(s) + SO_4^{2-} + OH^-$$
  
(not balanced) [M.L.N.R. 1992]

#### Solution:

$$S_2O_3^{2-} \longrightarrow 2SO_4^{2-}$$

Change in oxidation number of sulphur per molecule of  $S_2O_3^{2-} = 2 \times (6-2) = 8$ 

Change in oxidation number of Mn per molecule of  $MnO_4^- = 7 - 4 = 3$ 

No. of moles in 0.158 g of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 
$$\frac{0.158}{158}$$
 = 1 × 10<sup>-3</sup>  
No. of equivalents = 8 × 10<sup>-3</sup>

Normality of 0.1 M KMnO<sub>4</sub> solution = 0.1  $\times$  3 = 0.3 Let V mL of volume of KMnO<sub>4</sub> be required; then

$$\frac{V}{1000} \times 0.3 = 8 \times 10^{-3}$$

$$V = \frac{8}{0.3} \times 10^{-3} \times 10^{3}$$

$$= 26.7 \text{ mJ}$$

**Example 36.** 25 mL of  $H_2O_2$  solution were added to excess of acidified solution of KI. The iodine so liberated required 20 mL of 0.1 N  $Na_2S_2O_3$  for titration. Calculate the strength of  $H_2O_2$  in terms of normality, percentage and volume.

[M.L.N.R. 1996]

#### **Solution:**

or

20 mL of 0.1 N 
$$Na_2S_2O_3$$

= 20 mL of 0.1  $N I_2$  solution = 20 mL of 0.1  $N H_2O_2$  solution = 25 mL of 0.08  $N H_2O_2$  solution

Mass of H<sub>2</sub>O<sub>2</sub> in 100 mL solution = 
$$\frac{0.08\times17\times100}{1000} = 0.136 \text{ g}$$
 
$$\% = 0.136$$

68 g  $H_2O_2$  evolve oxygen at N.T.P. = 22400 mL 0.00136 g H<sub>2</sub>O<sub>2</sub> evolve oxygen at N.T.P.

$$= \frac{22400}{68} \times 0.00136 = 0.448$$
 The solution is of 0.448 volume.

**Example 37.** 0.5 g mixture of  $K_2Cr_2O_7$  and  $KMnO_4$  was treated with excess of KI in acidic medium. Iodine liberated required 100 cm<sup>3</sup> of 0.15 N sodium thiosulphate solution for titration. Find the per cent amount of each in the mixture.

[Roorkee 1995]

#### **Solution:**

Let 'a' g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> be present in the mixture.

Mass of KMnO<sub>4</sub> = 
$$(0.5 - a)$$
 g

Eq. mass of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> =  $\frac{\text{Mol. mass}}{6} = \frac{294}{6} = 49.0$ 

Eq. mass of KMnO<sub>4</sub> =  $\frac{\text{Mol. mass}}{5} = \frac{158}{5} = 31.6$ 

No. of equivalents of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> =  $\frac{a}{49.0}$ 

No. of equivalents of KMnO<sub>4</sub> =  $\frac{(0.5 - a)}{31.6}$ 

No. of equivalents of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in 100 cm<sup>3</sup> of 0.15 N solution

 $= \frac{100 \times 0.15}{1000} = 0.015$ Equivalents of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + Equivalents of KMnO<sub>4</sub>

≡ Equivalents of iodine  $\equiv$  Equivalents of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  $\frac{a}{49.0} + \frac{(0.5 - a)}{31.6} = 0.015$ 17.4a = 1.274a = 0.0732

% of 
$$K_2Cr_2O_7 = \frac{0.0732 \times 100}{0.5} = 14.64$$
  
% of  $KMnO_4 = 85.36$ 

### Some Miscellaneous Worked Problems

**Example 38.** Calculate the normality of a solution obtained by mixing 100 mL  $\frac{N}{10}$  H<sub>2</sub>SO<sub>4</sub>, 50 mL  $\frac{N}{2}$  HNO<sub>3</sub> and 25  $mL\frac{N}{5}HCl$  solutions.

#### Solution:

Let the final normality be N.

Total volume = 
$$(100 + 50 + 25) = 175$$
 mL  
So,  $175 \times N = N_1V_1 + N_2V_2 + N_3V_3$   
 $(H_2SO_4)$  (HNO<sub>3</sub>) (HCl)

$$= \left(100 \times \frac{1}{10}\right) + \left(50 \times \frac{1}{2}\right) + \left(25 \times \frac{1}{5}\right)$$

$$= (10 + 25 + 5) = 40$$

$$N = \frac{40}{175} = 0.2286$$

Hence, normality of solution = 0.2286 N

**Example 39.** 0.5 g of fuming  $H_2SO_4$  (oleum) is diluted with water. This solution is completely neutralised by 26.7 mL of 0.4 N NaOH. Find the percentage of free SO<sub>2</sub> in the sample solution.

#### **Solution:**

or

Oleum consists of SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>.

Let the mass of  $SO_2$  in the given sample of oleum be = x g Mass of  $H_2SO_4$  in the given sample of oleum = (0.5 - x) g

Eq. mass of 
$$SO_3 = \frac{80}{2} = 40$$
;  
No. of g equivalents of  $SO_3 = \frac{x}{40}$   
 $[2NaOH + SO_3 \longrightarrow Na_2SO_4 + H_2O$   
 $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O]$   
Eq. mass of  $H_2SO_4 = \frac{98}{2} = 49$   
No. of g equivalents of  $H_2SO_4 = \frac{(0.5 - x)}{49}$ 

Total no. of g equivalents = 
$$\frac{x}{40} + \frac{(0.5 - x)}{49}$$

26.7 mL of 0.4 N NaOH contain no. of equivalents of NaOH  $=\frac{0.4}{1000}\times26.7$ 

At equivalence point,

No. of g equivalents of NaOH = 
$$\frac{x}{40} + \frac{(0.5 - x)}{49}$$
  
So,  $\frac{0.4 \times 26.7}{1000} = \frac{49x + (40 \times 0.5 - 40x)}{40 \times 49}$   
 $x = \frac{0.9328}{9}$   
 $= 0.1036$   
Hence, % of free SO<sub>3</sub> =  $\frac{0.1036}{0.5} \times 100$   
 $= 20.72$ 

**Example 40.** 0.789 g of crystalline barium hydroxide is dissolved in water. For the neutralisation of this solution, 20 mL of  $\frac{N}{4}$  HNO<sub>3</sub> is required. How many molecules of water are present in one g mole of this base? [Ba = 137.4, O = 16.]N = 14, H = 11

#### Solution:

Let the molecular formula be  $Ba(OH)_2 \cdot xH_2O$ . Mol. mass of Ba(OH)<sub>2</sub>·xH<sub>2</sub>O = 137.4 + (2 × 16) + 2 × 1 + 18x= 171.4 + 18x

Eq. mass of Ba(OH)<sub>2</sub>·xH<sub>2</sub>O = 
$$\frac{171.4 + 18x}{2}$$
  
 $20 \text{ mL } \frac{N}{4} \text{ HNO}_3 = 20 \text{ mL } \frac{N}{4} \text{ Ba(OH)}_2 \cdot x\text{H}_2\text{O}$   
Amount of Ba(OH)<sub>2</sub>·xH<sub>2</sub>O =  $\frac{(171.4 + 18x)}{2 \times 4} \times \frac{20}{1000}$   
=  $\frac{171.4 + 18x}{400} \text{ g}$   
Amount of Ba(OH)<sub>2</sub>·xH<sub>2</sub>O = 0.789 g  
Hence,  $\frac{171.4 + 18x}{400} = 0.789$   
or  $171.4 + 18x = 0.789 \times 400$   
 $x = \frac{144.2}{18} = 8.01 \approx 8$ 

Thus, 8 water molecules are present in one g mole of the

Example 41. (i) What is the weight of sodium bromate and molarity of the solution necessary to prepare 85.4 mL of 0.672 N solution when the half reaction is

$$BrO_3^- + 6H^+ + 6e \longrightarrow Br^- + 3H_2O$$

(ii) What would be the weight as well as molarity if the half cell reaction is

$$2BrO_3^- + 12H^+ + 10e \longrightarrow Br_2 + 6H_2O$$

#### **Solution:**

(i) Molecular mass of NaBrO<sub>3</sub> = 
$$23 + 80 + (3 \times 16)$$
  
=  $151$ 

Each bromate ion takes up 6 electrons; therefore,

Eq. mass of NaBrO<sub>3</sub> = 
$$\frac{\text{Mol. mass}}{6} = \frac{151}{6}$$

Amount of NaBrO<sub>3</sub> in 85.5 mL 0.672 N solution

$$= \frac{0.672}{1000} \times \frac{151}{6} \times 85.5 = 1.446 \text{ g}$$

Molarity = 
$$\frac{\text{Normality}}{n} = \frac{0.672}{6} = 0.112 \text{ M}$$

(ii) Each bromate ion takes up 5 electrons; therefore,

Eq. mass of NaBrO<sub>3</sub> = 
$$\frac{\text{Mol. mass}}{5} = \frac{151}{5}$$

Amount of NaBrO<sub>3</sub> in 85.5 mL 0.672 N solution

$$= \frac{151}{5} \times \frac{0.672}{1000} \times 85.5$$

$$= 1.7352 \text{ g}$$
Molarity =  $\frac{\text{Normality}}{n} = \frac{0.672}{5} = 0.1344 \text{ M}$ 

Example 42. A piece of aluminium weighing 2.7 g is heated with 75 mL of  $H_2SO_4$  (sp. gr. 1.18, containing 24.7%  $H_2SO_4$  by mass). After the metal is carefully dissolved, the solution is diluted to 400 mL. Calculate the molarity of the free  $H_2SO_4$  in the resulting solution.

#### Solution:

Mass of 
$$H_2SO_4 = \frac{24.7}{100} \times 75 \times 1.18$$
  
= 21.8595 g

Reaction: 
$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2$$
  
 $2 \times 27 \quad 3 \times 98$ 

H<sub>2</sub>SO<sub>4</sub> required for dissolving 2.7 g Al

$$=\frac{3\times98}{2\times27}\times2.7=14.7 \text{ g}$$

 $H_2SO_4$  left unreacted = (21.8595 - 14.7) = 7.1595 g 7.1595 g  $H_2SO_4$  is present in 400 mL.

Amount of H<sub>2</sub>SO<sub>4</sub> present in one litre = 
$$\frac{7.1595}{400} \times 1000$$
 g = 17.898 g  
No. of g moles of H<sub>2</sub>SO<sub>4</sub> =  $\frac{17.898}{98}$  = 0.1826  
Hence, molarity of H<sub>2</sub>SO<sub>4</sub> = 0.1826 *M*

Example 43. 0.261 g of a sample of pyrolusite was heated with excess of HCl and the chlorine evolved was passed in a

solution of KI. The liberated iodine required 90 mL  $\frac{N}{30}$  Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Calculate the percentage of MnO<sub>2</sub> in the sample.

#### Solution:

$$\begin{array}{c} \text{MnO}_2 + 4\text{HCI} \longrightarrow \text{MnCI}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 \\ 2\text{KI} + \text{Cl}_2 \longrightarrow 2\text{KCI} + \text{I}_2 \\ 2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \\ 90 \text{ mL} \frac{N}{30} \text{Na}_2\text{S}_2\text{O}_3 \equiv 90 \text{ mL} \frac{N}{30} \text{ I}_2 \\ \equiv 90 \text{ mL} \frac{N}{30} \text{ Cl}_2 \\ \equiv 90 \text{ mL} \frac{N}{30} \text{ MnO}_2 \\ \text{Eq. mass of MnO}_2 = \frac{\text{Mol. mass}}{2} = \frac{87}{2} \\ \text{[Since change in O.N. is from 4 to 2]} \\ \text{Amount of MnO}_2 = \frac{87}{2 \times 30} \times \frac{90}{1000} = 0.1305 \text{ g} \\ \% \text{ of MnO}_2 = \frac{0.1305}{0.261} \times 100 = 50 \\ \end{array}$$

**Example 44.** Calculate the percentage of available chlorine in a given sample of bleaching powder from the following data:

3.55 g of bleaching powder when treated with acetic acid and excess of KI liberated iodine which required 60 mL of 0.5 N sodium thiosulphate solution.

#### **Solution:**

60 mL 0.5 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 60 mL 0.5 N I<sub>2</sub>  
= 60 mL 0.5 N Cl<sub>2</sub>  
Amount of chlorine = 
$$\frac{35.5 \times 0.5}{1000} \times 60$$
  
= 1.065 g  
% available chlorine =  $\frac{1.065}{3.55} \times 100$   
= 30.0

Example 45. 0.50 g of a mixture of  $K_2CO_3$  and  $Li_2CO_3$  requires 30 mL of a 0.25 N HCl solution for neutralisation. What is the percentage composition of the mixture?

**Solution:** 

Let x g of  $K_2CO_3$  be present in the mixture.

Mass of 
$$Li_2CO_3 = (0.50 - x)$$

No. of g equivalents of 
$$K_2CO_3 = \frac{x}{69}$$

No. of g equivalents of 
$$\text{Li}_2\text{CO}_3 = \frac{(0.50 - x)}{37}$$

No. of g equivalents in 30 mL of 0.25 N HCl

$$=\frac{\text{Normality} \times \text{Volume}}{1000} = \frac{0.25 \times 30}{1000} = \frac{3}{400}$$

At equivalence point,

$$\frac{x}{69} + \frac{(0.50 - x)}{37} = \frac{3}{400}$$
So,  $x = 0.48$ 

$$K_2CO_3 = 0.48 \text{ g; or } 96\%$$

$$Li_2CO_3 = 0.02 \text{ g; or } 4\%$$

**Example 46.** 0.804 g sample of iron ore was dissolved in acid. Iron was reduced to +2 state and it required 47.2 mL of  $0.112 \, N \, KMnO_4$  solution for titration. Calculate the percentage of iron and  $Fe_3O_4$  in the ore.

#### **Solution:**

The titration involves the conversion of ferrous into ferric.

$$5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \longrightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
  
 $47.2 \text{ mL of } 0.112 \text{ N KMnO}_4 = 47.2 \text{ mL of } 0.112 \text{ N Fe}^{2+} \text{ ions}$   

$$= \frac{47.2 \times 0.112 \times 55.5}{1000} = 0.2934$$

Mass of iron = 0.2934 g

% of iron in the ore = 
$$\frac{0.2934}{0.804} \times 100 = 36.49$$

$$3Fe \longrightarrow Fe_3O_4$$

$$(3 \times 55.5) \qquad (3 \times 55.5 + 64)$$

166.5 g of iron form 230.5 g of Fe<sub>3</sub>O<sub>4</sub>.

0.2934 g of iron will form = 
$$\frac{230.5}{166.5} \times 0.2934 = 0.406$$
 g % of Fe<sub>3</sub>O<sub>4</sub> in the ore =  $\frac{0.406}{0.804} \times 100 = 50.5$ 

**Example 47.** An equal volume of a reducing agent is treated separately with  $1\,M\,KMnO_4$  in acid, neutral and alkaline media. The volume of  $KMnO_4$  required are 20 mL in acid, 33.4 mL in neutral and 100 mL in alkaline media. Find out the oxidation state of manganese in each reaction product. Give the balanced equations for all the three half reactions. Find out the volume of  $1\,M\,K_2Cr_2O_7$  consumed, if the same volume of the reducing agent is treated in acid medium.

#### **Solution:**

Let  $N_1$ ,  $N_2$  and  $N_3$  be the normalities of 1 M KMnO<sub>4</sub> solution in acid, neutral and alkaline mediums, respectively.

$$20 \text{ mL } N_1 \equiv 33.4 \text{ mL } N_2 \equiv 100 \text{ mL } N_3$$

In acidic medium, the half reaction is:

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$$
  
1 M KMnO<sub>4</sub> = 5 N KMnO<sub>4</sub>

Thus, from above relation,

$$N_2 = \frac{20}{33.4} \times N_1 = \frac{20}{33.4} \times 5 \ N = 3 \ N$$

and

$$N_3 = \frac{20}{100} \times N_1 = \frac{20}{100} \times 5 \ N = 1 \ N$$

The equations in the three media are:

$$\begin{array}{ccc} MnO_{4}^{-} + 5e & \xrightarrow{Acid} & Mn^{2+} \\ \hline MnO_{4}^{-} + 3e & \xrightarrow{Neutral} & Mn^{4+} \\ \hline MnO_{4}^{-} + e & \xrightarrow{Alkaline} & Mn^{6+} \\ \end{array}$$

The balanced equations are:

$$MnO_4^- + 8H^+ + 5e \xrightarrow{Acid} Mn^{2+} + 4H_2O$$
 $MnO_4^- + 2H_2O + 3e \xrightarrow{Neutral} MnO_2 + 4OH^ MnO_4^- + e \xrightarrow{Alkaline} MnO_4^{2-}$ 

The balanced equation in the case of acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution can be written as:

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 3Cr^{3+} + 7H_2O$$
  
1  $M K_2Cr_2O_7 = 6 N K_2Cr_2O_7$ 

The volume required for the titration of the same volume of reducing agent with acidified  $K_2Cr_2O_7$  solution as follows:

20 mL 5 N KMnO<sub>4</sub> = V 6 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  

$$V = \frac{20 \times 5}{6} = 16.67 \text{ mL}$$

Example 48. 5 mL of 8 N nitric acid, 4.8 mL of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made upto 2 litres. 30 mL of this acid mixture exactly neutralise 42.9 mL of sodium carbonate solution containing one gram of Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O in 100 mL of water. Calculate the amount in grams of the sulphate ions in solution.

#### **Solution:**

Molecular mass of  $Na_2CO_3 \cdot 10H_2O = 286$ 

Equivalent mass of Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O = 
$$\frac{286}{2}$$
 = 143

100 mL solution of sodium carbonate contains = 1 g 1000 mL solution of sodium carbonate contains = 10 g

Normality of the solution = 
$$\frac{10}{143}$$

Applying the formula,

Normality of acid solution  $\times$  its volume

= Normality of sodium carbonate solution  $\times$  its volume

Normality of the acid solution = 
$$\frac{10 \times 42.9}{143 \times 30}$$
 = 0.1  
Let *V* mL be the volume of H<sub>2</sub>SO<sub>4</sub> taken.

$$8 \times 5 + 4.8 \times 5 + 34 \times V = 0.1 \times 2000$$

$$V = 4 \text{ mL}$$
Amount of  $SO_4^{2-} = \frac{\text{Normality} \times \text{eq. mass} \times \text{volume}}{1000}$ 

$$= \frac{34 \times 48 \times 4}{1000} = 6.528 \text{ g}$$

**Example 49.** 2.26 g of an ammonium salt were treated with 100 mL of normal NaOH solution and boiled till no more of ammonia gas was given off. The excess of NaOH solution left over required 60 mL normal sulphuric acid. Calculate the percentage of ammonia in the salt.

#### **Solution:**

60 mL normal  $H_2SO_4 \equiv 60$  mL normal NaOH Thus, (100-60) mL normal NaOH were consumed by ammonium salt.

So, 40 mL normal NaOH  $\equiv$  40 mL normal NH<sub>3</sub> Amount of NH<sub>3</sub> in 40 mL normal NH<sub>3</sub>

$$= \frac{\text{Eq. mass of NH}_3 \times 40}{1000} = \frac{17 \times 40}{1000} = 0.68$$

So, % of ammonia in the ammonium salt =  $\frac{0.68}{2.26} \times 100$ = 30.09

**Example 50.** In a sample of sodium carbonate, some sodium sulphate is also mixed. 1.25 g of this sample is dissolved and the volume made up to 250 mL. 25 mL of this solution neutralises  $20 \, \text{mL of} \, \frac{N}{10}$  sulphuric acid. Calculate the percentage of sodium carbonate in the sample.

#### **Solution:**

25 mL of sample solution neutralises = 20 mL  $\frac{N}{10}$  H<sub>2</sub>SO<sub>4</sub> 250 mL of sample solution will neutralise

$$= 200 \text{ mL } \frac{N}{10} \text{ H}_2\text{SO}_4$$

$$= 200 \text{ mL } \frac{N}{10} \text{ H}_2\text{SO}_4 = 200 \text{ mL } \frac{N}{10} \text{ Na}_2\text{CO}_3 \text{ solution}$$

$$= \frac{E \times N \times V}{1000}$$

$$= \frac{53 \times 200}{10 \times 1000} = 1.06$$
% of Na<sub>2</sub>CO<sub>3</sub> in the sample =  $\frac{1.06}{1.25} \times 100 = 84.9$ 

**Example 51.** 10 mL of a solution containing sulphuric acid and hydrochloric acid required 16 mL  $\frac{N}{8}$  caustic soda solution for neutralisation. On adding excess of barium chloride to 20 mL of the same solution of the mixture of the two acids, it gives 0.3501 g barium sulphate. What is the amount of hydrochloric acid per litre in the mixture of acids?

$$(Ba = 137.4, S = 32, O = 16, Cl = 35.5)$$

#### **Solution:**

Mol. mass of 
$$BaSO_4 = (137.4 + 32 + 64) = 233.4$$
  
 $H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl$   
98 g 233.4 g

233.4 g of BaSO<sub>4</sub> is obtained from = 98 g of H<sub>2</sub>SO<sub>4</sub>  
0.3501 g of BaSO<sub>4</sub> is obtained from = 
$$\frac{98}{233.4} \times 0.3501$$
  
= 0.147 g of H<sub>2</sub>SO<sub>4</sub>

20 mL of acid mixture contains 0.147 g of  $H_2SO_4$  So,10 mL of acid mixture contains 0.0735 g of  $H_2SO_4$ 

Amount of NaOH in 16 mL  $\frac{N}{8}$  NaOH solution  $= \frac{E \times N \times V}{1000}$  $= \frac{40 \times 16}{8 \times 1000} = 0.08 \text{ g}$ 

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$
  
98 g 2 × 40 = 80 g

Thus, 98 g of H<sub>2</sub>SO<sub>4</sub> require = 80 g of NaOH

$$0.0735$$
 g of H<sub>2</sub>SO<sub>4</sub> will require =  $\frac{80}{98} \times 0.0735$  g of NaOH

$$= 0.06$$
 g of NaOH

Let the amount of HCl in 10 mL acid mixture be = x g HCl + NaOH  $\longrightarrow$  NaCl + H<sub>2</sub>O

$$HC1 + NaOH \longrightarrow NaC1 + H_2O$$
  
36.5 g 40 g  
36.5 g HCl require = 40 g of NaOH

x g HCl will require =  $\frac{40}{36.5}$  x g of NaOH = 1.0958 x g of NaOH 1.0958x + 0.06 = 0.08

$$x = \frac{(0.08 - 0.06)}{1.0958} = 0.01825 \text{ g}$$

Amount of HCl present in one litre of the acid, solution

$$= \frac{0.01825 \times 1000}{10} = 1.825$$

**Example 52.** 1.6 g of pyrolusite ore was treated with 50 cm<sup>3</sup> of 1.0 N oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 cm<sup>3</sup> in a flask. 25 cm<sup>3</sup> of this solution when titrated with 0.1 N KMnO<sub>4</sub> required 32 cm<sup>3</sup> of the solution. Find the percentage of pure  $MnO_2$  in the sample and also the percentage of available oxygen. [Roorkee 1996]

#### **Solution:**

25 cm<sup>3</sup> of undecomposed oxalic acid required =  $32 \text{ cm}^3 0.1 \text{ N KMnO}_4 \text{ solution}$ 

Thus,  $250~{\rm cm}^3$  of undecomposed oxalic acid required

=  $320 \text{ cm}^3 0.1 \text{ N KMnO}_4 \text{ solution}$ 

 $= 32 \text{ cm}^3 \text{ 1 } N \text{ KMnO}_4 \text{ solution}$ 

 $= 32 \text{ cm}^3 1 N \text{ oxalic acid solution}$ 

Oxalic acid used by pyrolusite

= 
$$(50 - 32)$$
 cm<sup>3</sup> 1 N solution  
=  $18$  cm<sup>3</sup> 1 N solution  
=  $18$  cm<sup>3</sup> 1 N MnO<sub>2</sub> solution

Mass of MnO<sub>2</sub> = 
$$\frac{N \times E \times V}{1000} = \frac{1 \times 18 \times 87}{1000 \times 2} = 0.783$$
 g  
Percentage of MnO<sub>2</sub> =  $\frac{0.783}{1.6} \times 100 = 48.9$   
MnO<sub>2</sub>  $\longrightarrow$  MnO + O  
87 g 16 g  
Oxygen given by 0.783 g MnO<sub>2</sub> =  $\frac{16}{87} \times 0.783 = 0.144$  g  
% of available oxygen =  $\frac{0.144}{1.6} \times 100 = 9.0$ 

**Example 53.** A mixture of  $H_2C_2O_4$  and  $NaHC_2O_4$  weighing 2.02 g was dissolved in water and the solution made up to one litre. 10 mL of this solution required 3.0 mL of 0.1 N NaOH solution for complete neutralisation. In another experiment, 10 mL of same solution in hot dilute  $H_2SO_4$  medium required 4 mL of 0.1 N KMnO<sub>4</sub> for complete neutralisation. Calculate the amount of  $H_2C_2O_4$  and  $NaHC_2O_4$  in the mixture.

[I.I.T. 1990]

#### **Solution:**

Let mass of  $H_2C_2O_4$  present in the mixture be = a g in 1 litre and mass of  $NaHC_2O_4$  present in the mixture be = b g in 1 litre For acid base reaction

$$\begin{aligned} &H_2C_2O_4 + 2NaOH \longrightarrow Na_2C_2O_4 + 2H_2O \\ &Eq. \text{ mass of } H_2C_2O_4 = \frac{Mol. \text{mass}}{2} = \frac{90}{2} = 45 \\ &NaHC_2O_4 + NaOH \longrightarrow Na_2C_2O_4 + H_2O \\ &Eq. \text{ mass of } NaHC_2O_4 = \frac{Mol. \text{mass}}{1} = 112 \end{aligned}$$

Now.

Equivalents of  $H_2C_2O_4$  + Equivalents of  $NaHC_2O_4 = \frac{3 \times 0.1}{1000}$  in 10 mL solution in 10 mL solution

$$\frac{a \times 10}{45 \times 1000} + \frac{b \times 10}{112 \times 1000} = \frac{3 \times 0.1}{1000}$$

or 
$$112a + 45b = \frac{3 \times 0.1 \times 45 \times 112}{10} = 151.2$$
 ...(i)

For redox reaction

Eq. mass of 
$$H_2C_2O_4 = \frac{90}{2} = 45$$
;

Eq. mass of NaHC<sub>2</sub>O<sub>4</sub> = 
$$\frac{112}{2}$$
 = 56

(Change in oxidation number of carbon per molecule = 2;  $C_2^{3+} \longrightarrow 2C^{4+}$ )

Now,

or

Equivalents of  $H_2C_2O_4$  + Equivalents of  $NaHC_2O_4 = \frac{4 \times 0.1}{1000}$  in 10 mL solution in 10 mL solution

$$\frac{a \times 10}{45 \times 1000} + \frac{b \times 10}{56 \times 1000} = \frac{4 \times 0.1}{1000}$$

56a + 45b = 100.8 ...(ii)

Solving equations (i) and (ii),

$$a = 0.9 \text{ g}$$
 and  $b = 1.12 \text{ g}$ 

**Example 54.** A 3.0 g sample containing  $Fe_3O_4$ ,  $Fe_2O_3$  and an inert impure substance is treated with excess of KI solution in presence of dilute  $H_2SO_4$ . The entire iron is converted to  $Fe^{2+}$  along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the dilute solution requires 11.0 mL of 0.5 M  $Na_2S_2O_3$  solution to reduce the iodine present. A 50 mL of the diluted solution after complete extraction of iodine requires 12.8 mL of 0.25 M KMnO<sub>4</sub> solution in dilute  $H_2SO_4$  medium for oxidation of  $Fe^{2+}$ . Calculate the percentage of  $Fe_2O_3$  and  $Fe_3O_4$  in the original sample.

[LLT. 1996]

#### Solution:

Fe<sub>3</sub>O<sub>4</sub> is an equimolar mixture of Fe<sub>2</sub>O<sub>3</sub> and FeO. Thus, the sample contains Fe<sub>2</sub>O<sub>3</sub>, FeO and impurities. The amount of iodine liberated depends on the amount of Fe<sub>2</sub>O<sub>3</sub> and the entire iron is converted into Fe<sup>2+</sup>.

$$\begin{array}{c} -\mathrm{Fe_3O_4} + 2\mathrm{KI} + \mathrm{H_2SO_4} \longrightarrow 3\mathrm{FeO} + \mathrm{H_2O} + \mathrm{K_2SO_4} + \mathrm{I_2} \\ \mathrm{Fe_2O_3} + 2\mathrm{KI} + \mathrm{H_2SO_4} \longrightarrow 2\mathrm{FeO} + \mathrm{H_2O} + \mathrm{K_2SO_4} + \mathrm{I_2} \\ 5 \times 11.0 \ \mathrm{mL} \ \mathrm{of} \ 0.5 \ \mathit{M} \ \mathrm{Na_2S_2O_3} \equiv 55.0 \ \mathrm{mL} \ \mathrm{of} \\ 0.5 \ \mathit{N} \ \mathrm{Na_2S_2O_3} \ \mathrm{soln.} \\ \equiv 55.0 \ \mathrm{mL} \ \mathrm{of} \ 0.5 \ \mathit{N} \ \mathrm{Fe_2O_3} \ \mathrm{soln.} \\ \equiv 55.0 \ \mathrm{mL} \ \mathrm{of} \ 0.5 \ \mathit{N} \ \mathrm{Fe_2O_3} \ \mathrm{soln.} \\ = 27.5 \times 10^{-3} \ \mathrm{equivalent} \ \mathrm{Fe_2O_3} \ \mathrm{soln.} \\ = 13.75 \times 10^{-3} \ \mathrm{mole} \ \mathrm{Fe_2O_3} \\ 2 \times 12.8 \ \mathrm{mL} \ \mathrm{of} \ 0.25 \ \mathit{M} \ \mathrm{KMnO_4} \ \mathrm{soln.} \\ \equiv 25.6 \ \mathrm{mL} \ \mathrm{of} \ 1.25 \ \mathit{N} \ \mathrm{KMnO_4} \ \mathrm{soln.} \\ \equiv 25.6 \ \mathrm{mL} \ \mathrm{of} \ 1.25 \ \mathit{N} \ \mathrm{FeO} \ \mathrm{soln.} \\ \end{array}$$

= 25.6 mL of 1.25 N FeO soln.  
= 
$$32.0 \times 10^{-3}$$
 equivalent FeO  
=  $32.0 \times 10^{-3}$  mole FeO

Moles of FeO in 
$$Fe_3O_4 = 0.032 - 0.0275 = 0.0045$$
  
Mass of  $Fe_3O_4 = 0.0045 \times 232 = 1.044$  g

Moles of Fe<sub>2</sub>O<sub>3</sub> existing separately

$$= 0.01375 - 0.0045 = 0.00925$$
 Mass of Fe<sub>2</sub>O<sub>3</sub> = 0.00925 × 160 = 1.48 g  
% Fe<sub>3</sub>O<sub>4</sub> =  $\frac{1.044}{3}$  × 100 = 34.8  
% Fe<sub>2</sub>O<sub>3</sub> =  $\frac{1.48}{3}$  × 100 = 49.33

**Example 55.** Hydroxylamine reduces iron (III) according to the equation,

$$2NH_2OH + 4Fe^{3+} \longrightarrow N_2O(g) \uparrow + H_2O + 4Fe^{2+} + 4H^+$$

Iron (II) thus produced is estimated by titration with a standard permanganate solution. The reaction is:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

A 10 mL sample of hydroxylamine solution was diluted to one litre. 50 mL of this diluted solution was boiled with excess of iron (III) solution. The resulting solution required 12 mL of 0.02 M KMnO<sub>4</sub> solution for complete oxidation of iron (II).

Calculate the mass of hydroxylamine in one litre of the original solution.

#### **Solution:**

12 mL of 0.02 
$$M$$
 KMnO<sub>4</sub>  $\equiv$  12 mL of 0.1  $N$  KMnO<sub>4</sub>  $\equiv$  12 mL of 0.1  $N$  Fe<sup>2+</sup>  $\equiv$  12 mL of 0.1  $N$  NH<sub>2</sub>OH

Eq. mass of NH<sub>2</sub>OH = 
$$\frac{\text{Mol. mass}}{2} = \frac{33}{2} = 16.5$$

Mass of NH<sub>2</sub>OH in 12 mL of 0.1 N NH<sub>2</sub>OH soln.

$$= \frac{N \times E \times V}{1000} = \frac{0.1 \times 16.5 \times 12}{1000} = 0.0198 \text{ g}$$

50 mL of diluted solution contains  $NH_2OH = 0.0198$  g 1000 mL of diluted solution contains  $NH_2OH$ 

$$= \frac{0.0198}{50} \times 1000$$

10 mL of original solution contains  $NH_2OH = 0.396$  g 1000 mL of original solution contains  $NH_2OH$ 

$$= 100 \times 0.396 = 39.6 g$$

**Example 56.** A small amount of  $CaCO_3$  completely neutralises 525 mL of 0.1 N HCl and no acid is left in the end. After converting all calcium chloride to  $CaSO_4$ , how much plaster of Paris can be obtained? [Dhanbad 1991]

#### **Solution:**

525 mL of 0.1 N HCl = 525 mL of 0.1 N CaCl<sub>2</sub> = 525 mL of 0.1 N plaster of Paris

Molecular mass of plaster of Paris = 
$$CaSO_4 \cdot \frac{1}{2}H_2O$$
  
= 145

Equivalent mass of plaster of Paris =  $\frac{145}{2}$  = 72.5

Mass of plaster of Paris in 525 mL of 0.1 N solution

$$= \frac{N \times E \times V}{1000} = \frac{0.1 \times 72.5 \times 525}{1000}$$
$$= 3.806 \text{ g}$$

**Example 57.** 0.56 g of limestone was treated with oxalic acid to give  $CaC_2O_4$ . The precipitate decolourised 45 mL of 0.2 N KMnO<sub>4</sub> in acid solution. Calculate % of CaO in limestone.

#### **Solution:**

45 mL of 0.2 N KMnO<sub>4</sub> = 45 mL of 0.2 N CaC<sub>2</sub>O<sub>4</sub>  
= 45 mL of 0.2 N CaCO<sub>3</sub>  
= 45 mL of 0.2 N CaO  
Mass of CaO = 
$$\frac{N \times E \times V}{1000} = \frac{0.2 \times 28 \times 45}{1000}$$
  
= 0.252 g  
% of CaO in limestone =  $\frac{0.252}{0.56} \times 100$   
= 45

**Example 58.** A solution of 0.2 g of a compound containing  $Cu^{2+}$  and  $C_2O_4^{2-}$  ions on titration with 0.02 M KMnO<sub>4</sub> in presence of  $H_2SO_4$  consumes 22.6 mL oxidant. The resulting solution is neutralised by  $Na_2CO_3$ , acidified with dilute acetic acid and titrated with excess of KI. The liberated iodine required 11.3 mL of 0.05 M  $Na_2S_2O_3$  for complete reduction. Find out the mole ratio of  $Cu^{2+}$  and  $C_2O_4^{2-}$  in the compound.

[I.I.T. 1991]

**Solution:** 1st case: Only  $C_2O_4^{2-}$  ions are oxidised by  $KMnO_4$  solution.

Normality of KMnO<sub>4</sub> solution =  $0.02 \times 5 = 0.1 N$ 22.6 mL of 0.1 N KMnO<sub>4</sub> = 22.6 mL of 0.1 N C<sub>2</sub>O<sub>4</sub><sup>2-</sup> soln.

Mass of 
$$C_2O_4^{2-}$$
 ions =  $\frac{N \times E \times V}{1000} = \frac{N \times M \times V}{1000 \times 2}$  in the solution

No. of moles of 
$$C_2O_4^{2-}$$
 ions in the solution =  $\frac{N \times M \times V}{1000 \times 2 \times M}$   
=  $\frac{N \times V}{2000} = \frac{0.1 \times 22.6}{2000} = 11.3 \times 10^{-4}$ 

**2nd case :** Only  $Cu^{2+}$  ions are reduced by KI and iodine liberated is neutralised by  $Na_2S_2O_3$  solution.

Mass of Cu<sup>2+</sup> ions in the solution

$$= \frac{N \times E \times V}{1000} = \frac{N \times M \times V}{1000}$$

No. of moles of Cu<sup>2+</sup> ions in the solution

$$= \frac{N \times M \times V}{1000 \times M} = \frac{N \times V}{1000}$$
$$= \frac{0.05 \times 11.3}{1000} = 5.65 \times 10^{-4}$$

Molar ratio of 
$$\frac{Cu^{2+}}{C_2O_4^{2-}} = \frac{5.65 \times 10^{-4}}{11.3 \times 10^{-4}} = \frac{1}{2}$$

**Example 59.** 12 g of an impure sample of arsenious oxide was dissolved in water containing 7.5 g of sodium bicarbonate and the resulting solution was diluted to 250 mL. 25 mL of this solution was completely oxidised by 22.4 mL of a solution of iodine. 25 mL of this iodine solution reacted with same volume of a solution containing 24.8 g of sodium thiosulphate solution  $(Na_2S_2O_3\cdot5H_2O)$  in one litre. Calculate the percentage of arsenious oxide in the sample. (Atomic mass of As = 75)

[Roorkee 1999]

#### **Solution:**

:.

Normality of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln. = 
$$\frac{24.8}{248}$$
 = 0.1 *N*  
Applying  $N_1V_1 = N_2V_2$ 

Volume of As<sub>2</sub>O<sub>3</sub> soln. in NaHCO<sub>3</sub> × Normality of this soln. = Volume of iodine soln. × Normality of iodine soln.

$$25 \times N_1 = 22.4 \times 0.1$$
$$N_1 = \frac{22.4 \times 0.1}{25}$$

Amount of As<sub>2</sub>O<sub>3</sub> present in 250 mL of the solution

= 
$$N_1 \times \frac{\text{Equivalent mass of As}_2\text{O}_3}{1000} \times 250$$
  
=  $\frac{22.4 \times 0.1}{25} \times \frac{198}{4} \times \frac{250}{1000} = 1.1088 \text{ g}$ 

Percentage of 
$$As_2O_3 = \frac{1.1088}{12} \times 100 = 9.24$$

**Example 60.** Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of  $KMnO_4$  (20 mL) acidified with dilute  $H_2SO_4$ . The same volume of the  $KMnO_4$  solution is just decolourised by 10 mL of  $MnSO_4$  in neutral medium simultaneously forming a dark brown precipitate of hydrated  $MnO_2$ . The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute  $H_2SO_4$ . Write the balanced equations involved in the reactions and calculate the molarity of  $H_2O_2$ . [LLT. 2001]

Solution

(i) 
$$MnO_2 + Na_2C_2O_4 + 2H_2SO_4 \longrightarrow MnSO_4 + Na_2SO_4$$
  
ppt. 1 mole  $+ 2CO_2 + 2H_2O_4$ 

$$mM \text{ of } MnO_2 = mM \text{ of } Na_2C_2O_4 = 10 \times 0.2 = 2$$

(ii) 
$$2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 + K_2SO_4$$
  
 $2 \text{ mole}$  ppt.  $+ 2H_2O$ 

$$mM \text{ of } KMnO_4 = mM \text{ of } MnO_2 \times \frac{2}{5} = 2 \times \frac{2}{5} = \frac{4}{5}$$

(iii) 
$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4$$
  
2 mole 5 mole 5 mole 2 Mas  $O_4 + 2Mas O_4 + 8H_2O_4$ 

$$+ 2MnSO_4 + 8H_2O + 5O_2$$

:. 
$$mM ext{ of } H_2O_2 = mM ext{ of } KMnO_4 \times \frac{5}{2} = \frac{4}{5} \times \frac{5}{2} = 2$$

$$\therefore M \times 20 = 2$$

or 
$$M_{\rm H_2O_2} = \frac{2}{20} = 0.1 \ M$$

**Example 61.** The Mn<sub>3</sub>O<sub>4</sub> formed on strong heating of a sample of MnSO<sub>4</sub>·4H<sub>2</sub>O was dissolved in 100 cm<sup>3</sup> of 0.1 N

FeSO<sub>4</sub> containing dilute  $H_2SO_4$ . The resulting solution reacted completely with 50 cm<sup>3</sup> of KMnO<sub>4</sub> solution. 25 cm<sup>3</sup> of this KMnO<sub>4</sub> solution requires 30 cm<sup>3</sup> of 0.1 N FeSO<sub>4</sub> solution for complete reaction. Calculate the amount of MnSO<sub>4</sub>·4H<sub>2</sub>O in the sample. [Roorkee 2001]

#### Solution:

$$MnSO_4 \cdot 4H_2O \xrightarrow{Heat} Mn_3O_4$$

Mn<sub>3</sub>O<sub>4</sub> is dissolved in ferrous sulphate solution and is reduced from Mn<sup>(8/3)+</sup> to Mn<sup>2+</sup>. The excess of FeSO<sub>4</sub> is estimated by doing titration with KMnO<sub>4</sub> solution. The normality of KMnO<sub>4</sub> solution is determined by another ferrous sulphate solution.

For normality of KMnO<sub>4</sub> solution:

$$25 \times N = 30 \times 0.1$$
$$N = \frac{30 \times 0.1}{25} = \frac{3}{25}$$

Let the volume of unreacted FeSO<sub>4</sub> solution be V mL.

$$V \text{ mL of } 0.1 \text{ N FeSO}_4 = 50 \text{ mL of } \frac{3}{25} N \text{ KMnO}_4$$

or 
$$V = \frac{50 \times 3}{0.1 \times 25} = 60 \text{ mL}$$

$$\therefore$$
 Volume of FeSO<sub>4</sub> used for Mn<sub>3</sub>O<sub>4</sub> = (100 - 60) mL = 40 mL

40 mL of 0.1 N FeSO<sub>4</sub> 
$$\equiv$$
 40 mL of 0.1 N Mn<sub>3</sub>O<sub>4</sub>  
 $\equiv$  40 mL of 0.1 N MnSO<sub>4</sub>·4H<sub>2</sub>O

Mass of MnSO<sub>4</sub>·4H<sub>2</sub>O = 
$$\frac{E \times 0.1 \times 40}{1000} = \frac{E}{250}$$
 g

Equivalent mass of

MnSO<sub>4</sub>·4H<sub>2</sub>O = 
$$\frac{M}{\left(\frac{8}{3}-2\right)} = \frac{3M}{2} = \frac{3 \times 223}{2}$$

$$\therefore \text{ Mass of MnSO}_4 \cdot 4H_2O = \frac{3 \times 223}{2 \times 250}$$

$$= 1.338 g$$

# - • • • - PRACTICE PROBLEMS - •

### ■ Subjective Type Questions

- 1. What do you mean by volumetric analysis? How do you classify the reactions which are involved in volumetric analysis?
- 2. What is the principle of volumetric analysis? Derive the relationship  $N_1V_1 = N_2V_2$ .
- 3. What is equivalent mass? How do you calculate the equivalent masses of oxidising agents and reducing agents?
- **4.** Calculate the equivalent mass of potassium permanganate in acidic, basic and neutral mediums.
- 5. Define the following terms:
  - (a) Standard solution (b) Normal solution (c) Indicator

- **6.** What do you mean by molarity and normality of the solution? How are these related?
- 7. Write short notes on:
  - (i) Iodimetry (ii) Iodometry (iii) Kjeldahl's process
- 8. Name the two common indicators used in acid-base titrations. How is a mixture containing NaOH and Na<sub>2</sub>CO<sub>3</sub> analysed by titration?
- 9. 12 mL of 0.25 N sulphuric acid is neutralised with 15 mL of sodium hydroxide solution on titration. Calculate the normality of sodium hydroxide solution.
- **10.** What will be the volume of *N*/10 solution of oxalic acid obtained by dissolving 63 g of oxalic acid?

- 11. If 1.26 g of oxalic acid is dissolved in 250 mL of solution, find its normality. The equivalent mass of oxalic acid is 63.
- **12.** 50 mL of 0.2 N KMnO<sub>4</sub> is required for complete oxidation of 0.45 g of anhydrous oxalic acid. Calculate the normality of oxalic acid solution.
- 13. 30 mL of sodium carbonate solution is mixed with 20 mL of 0.8 N sulphuric acid. The resultant solution needed 20 mL of 0.7 N hydrochloric acid solution for complete neutralisation. Determine the strength of the sodium carbonate in grams per litre. (Take sodium carbonate to be anhydrous).
- 14. Find the equivalent mass of  $H_3PO_4$  in the reaction  $Ca(OH)_2 + H_3PO_4 \longrightarrow CaHPO_4 + 2H_2O$ (At. mass H = 1, O = 16, P = 31, Ca = 40)
- **15.** 316 g of sodium thiosulphate was dissolved in water and made up to 250 mL. What is the normality of the solution?
- **16.** Calculate the equivalent mass of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O and KBrO<sub>3</sub> with the help of the following equations:
  - (i)  $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$
  - (ii)  $BrO_3^- + 6H^+ + 6e \longrightarrow Br^- + 3H_2O$
- 17. 0.25 g of an oxalate salt was dissolved in 100 mL of water. 10 mL of this solution required 8 mL of N/20 KMnO<sub>4</sub> for its oxidation. Calculate the percentage of oxalate in the salt.
- 18. 1.13 g of an ammonium sulphate were treated with 50 mL of normal NaOH solution and boiled till no more ammonia was given off. The excess of the alkali solution left over was titrated with normal H<sub>2</sub>SO<sub>4</sub>. The volume required was 30 mL. Find out the percentage of NH<sub>3</sub> in the salt.
- 19. The normality of the mixture of HCl and H<sub>2</sub>SO<sub>4</sub> solution is N/5. 0.287 g of AgCl is obtained when 20 mL of this solution is treated with excess of AgNO<sub>3</sub>. Calculate the percentage of both the acids in the mixture.
- 20. 1.17 g of an impure sample of oxalic acid was dissolved and made up to 200 mL with water. 10 mL of this solution in acid medium required 8.5 mL of a solution of potassium permanganate containing 3.16 g per litre of oxidation. Calculate percentage purity of oxalic acid.
- 21. What amount of silver chloride will be obtained when 20 mL N/20 HCl is made to react with excess of AgNO<sub>3</sub>?
- 22. 1.0 g carbonate of a metal was dissolved in 50 mL N/2 HCl solution. The resulting liquid required 25 mL of N/5 NaOH solution to neutralise it completely. Calculate the equivalent mass of the metal carbonate.
- 23. 0.35 g of a metal was dissolved in 50 mL *N*-acid. The whole solution then required 20.85 mL of normal alkaline solution to neutralise the excess of the acid. Calculate the equivalent mass of the metal.
- 24. 2.650 g of anhydrous sodium carbonate are dissolved in water and the solution made up to 500 mL. On titration 50 mL of this solution neutralises 50 mL of a solution of sulphuric acid. How much water should be added to 450 mL of this acid as to make it exactly N/12?
- 25. Two acids A and B are titrated separately each time with 25 mL of N Na<sub>2</sub>CO<sub>3</sub> solution and require 10 mL and 40 mL respectively for complete neutralisation. What volume of A and B would you mix to produce one litre of normal acid solution?

- **26.** 1.64 g of a mixture of calcium carbonate and magnesium carbonate were dissolved in 50 mL of 0.8 N hydrochloric acid. The excess of the acid required 16 mL N/4 sodium hydroxide solution for neutralisation. Find out the percentage composition of the mixture of two carbonates.
- 27. What weight of zinc carbonate can just neutralise 300 mL N/10 sulphuric acid? (At. mass of Zn = 65.0)
- 28. 20 mL N/2 HCl, 60 mL N/10 H<sub>2</sub>SO<sub>4</sub> and 150 mL N/5 HNO<sub>3</sub> are mixed. Determine the normality of the mixture of the acids in solution.
- **29.** A sample of hydrochloric acid contains 20% of hydrochloride by mass. How many grams of this acid sample is necessary to completely interact with 50 g of calcium carbonate?
- **30.** 30 mL of *N*/10 HCl are required to neutralise 50 mL of a sodium carbonate solution. How many mL of water must be added to 30 mL of this solution so that the solution obtained may have a concentration equal to *N*/50?
- 31. 2.65 g of diacidic base was dissolved in water and made up to 500 mL. 20 mL of this solution completely neutralised 12 mL of N/6 HCl. Find out the equivalent mass and molecular mass of the base.
- 32. In a sample of sodium carbonate some sodium sulphate is mixed. 2.50 g of this sample is dissolved and the volume made up to 500 mL. 25 mL of this solution neutralises 20 mL of N/10 sulphuric acid. Calculate the percentage of sodium carbonate in the sample.
- 33. Some amount of NH<sub>4</sub>Cl was boiled with 50 mL of 0.75 N NaOH solution till the reaction was complete. After the completion of the reaction, 10 mL of 0.75 N H<sub>2</sub>SO<sub>4</sub> were required for the neutralisation of the remaining NaOH. Calculate the amount of NH<sub>4</sub>Cl taken.
- 34. 25 mL of a mixed solution of sodium carbonate and sodium bicarbonate required 10 mL of N/20 HCl when titrated in the presence of phenolphthalein but 25 mL of the same when titrated separately in presence of methyl orange required 25 mL of N/10 HCl. Calculate the amount of anhydrous sodium carbonate and bicarbonate in grams per litre of the solution.
- 35. 4 g of a mixture of NaCl and Na<sub>2</sub>CO<sub>3</sub> were dissolved in water and volume made up to 250 mL. 15 mL of this solution required 50 mL of N/10 HCl for complete neutralisation. Calculate the percentage composition of the original mixture.
- 36. 40 mL of a mixture of Na<sub>2</sub>CO<sub>3</sub> and NaOH when titrated against N/10 HCl, the end point with phenolphthalein was reached at 25 mL of HCl and at this stage methyl orange was added, the quantity of acid further required for second end point was 5 mL. Calculate the amount of Na<sub>2</sub>CO<sub>3</sub> and NaOH in g/L of the solution.
- 37. Find out the percentage of oxalate in a given sample of an oxalate salt of which when 0.3 g were dissolved in 100 mL of water required 90 mL of N/20 KMnO<sub>4</sub> solution for complete oxidation.
- **38.** A 1.0 g sample of H<sub>2</sub>O<sub>2</sub> solution containing 'x' per cent by weight requires x mL of a KMnO<sub>4</sub> solution for complete oxidation under acidic conditions. Calculate the normality of the KMnO<sub>4</sub> solution.

- 39. 25 g of a sample of ferrous sulphate was dissolved in water containing dilute H<sub>2</sub>SO<sub>4</sub> and the volume made up to one litre.
  25 mL of this solution required 20 mL of N/10 KMnO<sub>4</sub> solution for complete oxidation. Calculate the percentage of FeSO<sub>4</sub>·7H<sub>2</sub>O in the sample.
- **40.** (i) A sample of MnSO<sub>4</sub>:4H<sub>2</sub>O is strongly heated in air. The residue is Mn<sub>3</sub>O<sub>4</sub>.
  - (ii) The residue is dissolved in 100 mL of 0.1 N FeSO<sub>4</sub> containing dilute H<sub>2</sub>SO<sub>4</sub>.
  - (iii) The solution reacts completely with 50 mL of KMnO<sub>4</sub> solution.
  - (iv) 25 mL of KMnO<sub>4</sub> used in step (iii) required 30 mL of 0.1 N FeSO<sub>4</sub> solution for complete reaction.

Find the amount of  $MnSO_4$ · $4H_2O$  present in the sample. (At. mass of Mn = 55)

- 41. A sample of KCl is contaminated with NaCl. 4.176 g of the sample is dissolved in distilled water and the solution is made to 500 mL. 25 mL of the above solution required 27.50 mL of a solution of silver nitrate (normality factor 0.115) to react completely with it. Calculate the percentage contamination of the sample.
- **42.** Mercuric iodate  $[Hg_5(IO_6)_2]$  reacts with a mixture of KI and HCl according to the equation:

$$Hg_5(IO_6)_2 + 34KI + 24HC1 \longrightarrow 5K_2HgI_4 + 8I_2 + 24KC1 + 12H_2O$$

The liberated iodine is titrated with  $Na_2S_2O_3$  solution, 1.0 mL of which is equivalent to 0.0499 g of  $CuSO_4$ ·5H<sub>2</sub>O. What volume (in mL) of the  $Na_2S_2O_3$  solution will be required to react with iodine liberated from 0.7245 g of  $Hg_5(IO_6)_2$ ? [Hg = 200.5, Cu = 63.5, I = 127]

[Hint:  $1448.5 \text{ g Hg}_5(IO_6)_2 \equiv 8I_2 \equiv 16\text{CuSO}_4.5\text{H}_2\text{O}$ 

So, 0.7245 g 
$$Hg_5(IO_6)_2 \equiv \frac{16 \times 249.5 \times 0.7245}{1448.5}$$
 g  $CuSO_4 \cdot 5H_2O$  0.0499 g  $CuSO_4 \cdot 5H_2O \equiv 1$  mL of the given  $Na_2S_2O_3$ ]

- 43. 5.0 g of bleaching powder was suspended in water and volume made up to half a litre. 20 mL of this suspension when acidified with acetic acid and treated with excess of KI solution liberated iodine which required 20 mL of a decinormal hypo solution for titration. Calculate percentage of available chlorine in bleaching powder. [Roorkee 1990]
- **44.** To a solution of excess of KI in dilute H<sub>2</sub>SO<sub>4</sub>, 25 mL of an unknown solution of KMnO<sub>4</sub> were added. The liberated iodine was exactly reduced by 42.5 mL of *N*/10 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. Calculate the concentration of KMnO<sub>4</sub> solution.
- 45. In 20 mL of a solution of HCl, 3 g of CaCO<sub>3</sub> were dissolved, 0.5 g of CaCO<sub>3</sub> being left undissolved. Find out the strength of this solution in terms of (i) normality and (ii) g/L. Find the volume of this acid which would be required to make 1 litre of normal solution of this acid.
- **46.** 1.0 litre of a solution contains 5.3 g of Na<sub>2</sub>CO<sub>3</sub> and 8 g of NaOH. 20 mL of this solution are taken and titrated against *N*/10 HCl using separately (a) methyl orange as an indicator and (b) phenolphthalein as an indicator. What will be the titre values in these two cases?

- **47.** To 20 mL of a copper solution after necessary treatment were added excess of KI and the liberated iodine required 11.2 mL decinormal solution of hypo. Express the strength of the original solution in grams of copper per litre of the solution.
- **48.** 10 g of a commercial sample of copper sulphate were dissolved in water and the volume made up to 500 mL. 25 mL of this solution was treated with excess of KI and the liberated iodine required 30 mL of *N*/12 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. Calculate the percentage of copper in the sample.
- **49.** 0.28 g of a commercial sample of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was dissolved in water. Excess of KI was added to it along with dilute H<sub>2</sub>SO<sub>4</sub>. Iodine liberated was then titrated against sodium thiosulphate solution containing 24.82 g of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O per litre. The thiosulphate solution required was 50 mL. Find the percentage purity of the sample of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.
- **50.** A mixture containing KCl and NaCl was dissolved and total halide was determined by titration with silver nitrate. A sample weighing 0.3250 g required 51 mL of 0.1 N solution.

  Calculate the percentage of each salt in the sample.
- 51. 1.355 g of pyrolusite sample are added to 50 mL of 1 N oxalic acid solution containing sulphuric acid. After the reaction is completed, the contents are transferred to a measuring flask and the volume made up to 200 mL. 20 mL of this solution is titrated against KMnO<sub>4</sub> solution whose strength is 2 g/L and 31.6 mL of KMnO<sub>4</sub> solution are required. Calculate the percentage purity in the given sample of pyrolusite.
- 52. 0.5 g of bleaching powder was suspended in water an excess of KI added. On acidifying with dilute H<sub>2</sub>SO<sub>4</sub> iodine was liberated which required 50 mL of N/10 hyposolution. Calculate the percentage of available chlorine in bleaching powder.
- **53.** A compound contains C = 48% and H = 8%. On treating 0.48 g of the compound by Kjeldahl's method, the ammonia liberated required 19.2 mL of *N*/2 sulphuric acid for complete reaction. Determine the empirical formula of the compound.
- 54. 0.6 g of an organic compound was analysed. The ammonia thus produced was absorbed in 90 mL N/9 H<sub>2</sub>SO<sub>4</sub>. The remaining acid required 20 mL 0.1 N NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.
- 55. 0.95 g of an organic compound after being digested with H<sub>2</sub>SO<sub>4</sub> was boiled with excess of NaOH. The liberated ammonia was absorbed in 100 mL N H<sub>2</sub>SO<sub>4</sub>. The acid left required 62.5 mL of N NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.
- 56. Calculate the number of oxalic acid molecules in 100 mL of 0.02 N oxalic acid solution. [Roorkee 1991]

[**Hint**: Molarity = 
$$\frac{0.02}{2}$$
 = 0.01 M

No. of molecules in one molar solution =  $6.02 \times 10^{23}$ No. of molecules in 100 mL of 0.01 *M* oxalic acid solution

$$= \frac{0.01 \times 6.02 \times 10^{23}}{1000} \times 100$$
$$= 6.02 \times 10^{20}$$

**57.** How much water should be added to 50 mL of 0.1 N HCl in order to get 0.04 N solution?

- **58.** If 40 mL of 0.1 N KOH is mixed 60 mL of 0.05 N HCl, what will be the normality of the resulting solution? What will be the normality of salt formed after the reaction?
- 59. 1.26 g of a dibasic acid were dissolved in water and made up to 200 mL. 20 mL of this solution were completely neutralised by 10 mL of N/5 caustic soda solution. Calculate the equivalent mass and molecular mass of the acid.
- **60.** What will be the normality of solution obtained by mixing 20 mL of 0.5 N hydrochloric acid, 60 mL of 0.1 N sulphuric acid and 150 mL of 0.2 N nitric acid?
- 61. 3.0 g of a sample of impure ammonium chloride were boiled with excess of caustic soda solution. Ammonia gas so evolved was passed into 120 mL of N/2 H<sub>2</sub>SO<sub>4</sub>. 28 mL of N/2 NaOH were required to neutralise residual acid. Calculate the percentage of purity of the given sample of ammonium chloride.

| **Hint**: (120 - 28) mL N/2 H<sub>2</sub>SO<sub>4</sub> = 92 mL N/2 NH<sub>4</sub>Cl

- **62.** How much water should be added to 100 mL of 2.5 N H<sub>2</sub>SO<sub>4</sub> to make it normal solution?
- **63.** 2.20 g of an ammonium salt were boiled with 75 mL of *N* NaOH till the emission of ammonia gas ceased. The excess of unused NaOH solution required 70 mL of *N*/2 sulphuric acid for neutralisation. Calculate the percentage of ammonia in the salt.
- **64.** 3.45 g of a metallic carbonate were mixed with 240 mL of *N*/4 HCl. The excess acid was neutralised by 50 mL of *N*/5 KOH solution. Calculate the equivalent mass of the metal. [Hint: Equivalent mass of metal carbonate

$$= \frac{3.45 \times 4 \times 1000}{200} = 69$$
Equivalent mass of metal = 69 - eq. mass of carbonate =  $(69 - 30) = 39$ ]

- **65.** (a) 2 g of a metal carbonate were dissolved in 50 mL of *N* HCl. 100 mL of 0.1 *N* NaOH were required to neutralise the resultant solution. Calculate the equivalent mass of the metal carbonate.
  - (b) How much water should be added to 75 mL of 3 N HCl to make it a normal solution?
- 66. Upon mixing 45.0 mL of 0.25 *M* lead nitrate solution with 25 mL of 0.1 *M* chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the molar concentrations of the species left behind in the final solution. Assume that lead sulphate is completely insoluble. [I.I.T. 1993]

[Hint: The reaction is:

$$3Pb(NO_3)_2 + Cr_2(SO_4)_3 \longrightarrow 3PbSO_4 + 2Cr(NO_3)_3$$
  
3 moles 1 mole 3 moles 2 moles  
No. of moles of  $Pb(NO_3)_2 = 45 \times 10^{-3} \times 0.25$   
=  $11.25 \times 10^{-3}$  mole

No. of moles of  $Cr_2(SO_4)_3 = 25 \times 10^{-3} \times 0.1 = 2.5 \times 10^{-3}$  mole Thus,  $Cr_2(SO_4)_3$  has limiting concentration. It shall be consumed fully and the number of moles of lead sulphate produced will be

$$= 3 \times 2.5 \times 10^{-3} = 7.5 \times 10^{-3} \text{ mole}$$
No. of moles of lead nitrate left =  $11.25 \times 10^{-3} - 7.5 \times 10^{-3}$   
=  $3.75 \times 10^{-3}$  mole  
Total volume =  $(45.0 + 25.0) = 70$  mL or  $70 \times 10^{-3}$  litre

Molarity = 
$$\frac{3.75 \times 10^{-3}}{70 \times 10^{-3}}$$
 = 0.0536 *M*  
No. of moles of Cr(NO<sub>3</sub>)<sub>3</sub> formed = 2 × 2.5 × 10<sup>-3</sup>

of moles of Cr(NO<sub>3</sub>)<sub>3</sub> formed = 
$$2 \times 2.5 \times 10^{-3}$$
  
=  $5 \times 10^{-3}$  mole  
Molarity =  $\frac{5 \times 10^{-3}}{70 \times 10^{-3}}$  = 0.0714 M

Pb(NO<sub>3</sub>)<sub>2</sub> and Cr(NO<sub>3</sub>)<sub>3</sub> will be present in solution in ionic form.

Thus, 
$$[Pb^{2+}] = 0.0536 M$$

$$[Cr^{3+}] = 0.0714 M$$

$$[NO_3^-] = (2 \times 0.0536) + (3 \times 0.0714)$$

$$= 0.3214 M$$

67. A sample of hydrazine sulphate (N<sub>2</sub>H<sub>6</sub>SO<sub>4</sub>) was dissolved in 250 mL of water. 10 mL of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ions formed were estimated and it required 10 mL of 0.04 *M* potassium permanganate solution. Estimate the amount of hydrazine sulphate dissolved in 250 mL of the solution. Reactions:

$$4Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4Fe^{2+} + 4H^+ 
MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O 
[M.L.N.R. 1993]$$

[Hint: See Example 34]

**68.** In an ore the only oxidisable material is  $Sn^{2+}$ . This ore is titrated with a dichromate solution containing 2.5 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 0.50 litre. A 0.40 g of sample of the ore required 10.0 cm<sup>3</sup> of the titrant to reach equivalent point. Calculate the percentage of tin in ore. (K = 39.1, Cr = 52, Sn = 118.7)

[Roorkee 1993]

[Hint: Mol. mass of 
$$K_2Cr_2O_7 = 2 \times 39.1 + 2 \times 52 + 7 \times 16$$
  
=  $78.2 + 104.0 + 112.0$   
=  $294.2$   
Eq. mass of  $K_2Cr_2O_7 = \frac{294.2}{6} = 49.03$ 

Normality of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution 
$$=\frac{2.5}{49.03} \times \frac{1000}{500} = \frac{5}{49.03} N$$

10 mL
$$\frac{5}{49.03}$$
 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> = 10 mL $\frac{5}{49.03}$  N stannous ion

Eq. mass of 
$$\text{Sn}^{2+} = \frac{118.7}{2} = 59.35$$

Amount of Sn in the sample = 
$$\frac{5}{49.03} \times \frac{59.35}{1000} \times 10$$
  
= 0.0605 g

Percentage of Sn in the ore 
$$= \frac{0.0605}{0.40} \times 100 = 15.125$$
]

- 69. 2.26 g of impure ammonium chloride were boiled with 100 mL of N NaOH solution till no more ammonia was given off. The excess of NaOH solution left over required 30 mL 2 N H<sub>2</sub>SO<sub>4</sub> for neutralisation. Calculate the percentage purity of the salt. [H = 1; N = 14; O = 16; Na = 23; S = 32; Cl = 35.5]
- **70.** Metallic tin in the presence of HCl is oxidised by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution to stannic chloride. What volume of decinormal dichromate solution would be reduced by 1 g of Sn?

[M.L.N.R. 1994]

[Hint: 
$$3Sn + 2K_2Cr_2O_7 + 28HCl \longrightarrow 3SnCl_4 + 4KCl + 4CrCl_3  $3 \times 118.7 \text{ g} \quad 2 \times 294 \text{ g} \quad + 14H_2O$$$

$$K_2Cr_2O_7$$
 required for 1 g of  $Sn = \frac{2 \times 294}{3 \times 118.7} = 1.65$  g]

71. A sample containing 0.4775 g of (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and inert materials was dissolved in water and made strongly alkaline with KOH which converted NH<sub>4</sub> to NH<sub>3</sub>. The liberated ammonia was distilled into exactly 50.0 mL of 0.05035 M H<sub>2</sub>SO<sub>4</sub>. The excess H<sub>2</sub>SO<sub>4</sub> was back titrated with 11.3 mL of 0.1214 M NaOH. Calculate: (i) percentage of N, (ii) percentage of  $(NH_4)_2C_2O_4$ .

[At. mass of nitrogen = 14.0078; Mol. mass of  $(NH_4)_2C_2O_4$ =124.101[M.L.N.R. 1994]

[**Hint**: 11.3 mL 0.1214 M NaOH = 11.3 mL 0.1214 N NaOH  $\equiv 11.3 \text{ mL } 0.1214 \text{ N } \text{H}_2\text{SO}_4 = 1.3718 \text{ meq. } \text{H}_2\text{SO}_4$ 

H<sub>2</sub>SO<sub>4</sub> acid used for neutralisation of NH<sub>2</sub>

$$= (5.035 - 1.3718) = 3.663 \text{ meq.}$$
  
 $= 3.663 \text{ meq. NH}_3$ 

Amount of ammonium oxalate =  $3.663 \times 10^{-3} \times \text{Eq.}$  mass

= 
$$3.663 \times 10^{-3} \times \frac{124.10}{2}$$
  
=  $0.2273$  g]

72. A 0.5 g sample containing MnO<sub>2</sub> is treated with HCl liberating Cl<sub>2</sub>. The Cl<sub>2</sub> is passed into a solution of KI and 30.0 cm<sup>3</sup> of 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> are required to titrate the liberated iodine. Calculate the percentage of MnO<sub>2</sub> in the sample.

[Roorkee 1994]

[Hint: 30.0 mL 0.1 
$$M$$
 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 30.0 mL 0.1  $N$  Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  
= 30.0 mL 0.1  $N$  Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  
= 30.0 mL 0.1  $N$  Cl<sub>2</sub>  
= 30.0 mL 0.1  $N$  MnO<sub>2</sub>  
Amount of MnO<sub>2</sub> present =  $\frac{N \times E \times V}{1000}$   
=  $\frac{1}{10} \times \frac{87}{2} \times \frac{30}{1000}$   
% MnO<sub>2</sub> =  $\frac{87 \times 30 \times 100}{10 \times 2 \times 1000 \times 0.5} = 26.1$ ]

- 73. 5.3 g of a diacidic base was dissolved in water and made up to 1000 mL. 20 mL of this solution was completely neutralised by 24 mL of N/12 hydrochloric acid solution. Calculate the equivalent mass and molecular mass of the base.
- 74. 3.2 g of a mixture of calcium carbonate and sodium chloride was dissolved in 100 mL of 1.02 N HCl. After the reaction the solution was filtered and after separating the precipitate the volume was raised to 200 mL. 20 mL of this solution required 25 mL N/5 caustic soda solution for neutralisation. Find out the percentage of calcium carbonate in the mixture.
- 75. 4 g of a mixture of Na<sub>2</sub>SO<sub>4</sub> and anhydrous Na<sub>2</sub>CO<sub>3</sub> were dissolved in pure water and volume made up to 250 mL. 20 mL of this solution required 25 mL of N/5 H<sub>2</sub>SO<sub>4</sub> for complete neutralisation. Calculate the percentage composition of the mixture.
- **76.** A 1.2 g mixture of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> was dissolved in water to form 100 cm<sup>3</sup> of a solution. 20 cm<sup>3</sup> of this solution required 40 cm<sup>3</sup> of 0.1 N·HCl for neutralisation. Calculate the mass of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> in the mixture. [Roorkee 1997]

77. One litre of a mixture of  $O_2$  and  $O_3$  at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 mL of M/10 sodium thiosulphate solution for titration. What is the weight per cent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture? [L.I.T. 1997]

**[Hint:** Let the total moles of  $O_2$  and  $O_3$  in the mixture be n.

Applying 
$$PV = nRT$$

$$1 \times 1 = n \times 0.0821 \times 273$$

$$n = 0.044 \text{ mole}$$

$$Moles of O_3 = \text{moles of } I_2$$

$$= 1/2 \text{ moles of } Na_2S_2O_3$$

$$= \frac{1}{2} \times \frac{1}{10} \times \frac{40}{1000}$$

$$= 0.002 \text{ mole}$$

Moles of 
$$O_2$$
 in the mixture = 0.044 - 0.002 = 0.042 mole

Mass of  $O_2$  = 0.042 × 32 = 1.344 g

Mass of  $O_3$  = 0.002 × 48 = 0.096 g

%  $O_3$  =  $\frac{0.096}{1.44}$  × 100 = 6.6

No. of photons required to decompose 0.002 mole of ozone

 $= 0.002 \times 6.02 \times 10^{23} = 1.204 \times 10^{21}$ 

- **78.** 20 mL of a solution containing 0.2 g of impure sample of  $H_2O_2$ reacts with 0.316 g of KMnO<sub>4</sub> (acidic). Calculate:
  - (a) Purity of H<sub>2</sub>O<sub>2</sub>
  - (b) Volume of dry O<sub>2</sub> evolved at 27°C and 750 mm pressure.
- 79. Five gram of copper alloy was dissolved in a litre of dilute H<sub>2</sub>SO<sub>4</sub>. 20 mL of this solution was titrated iodometrically and it required 20 mL of a hypo solution. 20 mL of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> which contained 2.4 g per litre, in presence of H<sub>2</sub>SO<sub>4</sub> and excess of KI, required 30 mL of the same hypo solution. Calculate the % purity of copper in the alloy.
- How many millilitres of 0.5 M H<sub>2</sub>SO<sub>4</sub> are needed to dissolve 0.5 g of copper (II) carbonate? [I.I.T. 1999]

[Hint: 
$$N_1V_1 = N_2V_2$$
]

$$N_1$$
 = Normality of H<sub>2</sub>SO<sub>4</sub> = 0.5 × 2 = 1 N

$$V_1$$
 = Vol. of H<sub>2</sub>SO<sub>4</sub>

$$N_2$$
 = Normality of copper (II) carbonate =  $\frac{0.5 \times 2}{123.5} N$ 

 $V_2$  = Volume of copper (II) carbonate = 1000 mL

Thus, 
$$1.0 \times V_1 = \frac{0.5 \times 2}{123.5} \times 1000$$
  
or  $V_1 = 8.09 \text{ mL}$ 

81. An aqueous solution containing 0.10 g KIO<sub>3</sub> (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated iodine consumed 45.0 mL of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.

[Hint: 
$$2KIO_3 + 10KI + 12HCI \longrightarrow 12KC1 + 6I_2 + 6H_2O$$
  
 $[2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6] \times 6$ 

$$2KIO_3 + 10KI + 12Na_2S_2O_3 + 12HCl \longrightarrow 12KCl + 12NaI \\ 2 \ mole \qquad \qquad 12 \ mole \qquad \qquad + 6Na_2S_4O_6 + 6H_2O$$

No. of moles of KIO<sub>3</sub> = 
$$\frac{0.10}{214}$$
  
No. of moles of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> required for  $\frac{0.10}{214}$  mole of KIO<sub>3</sub> =  $\frac{12}{2} \times \frac{0.10}{214} = \frac{0.60}{214}$ 

Molarity of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 
$$\frac{0.6}{214} \times \frac{1000}{45} = 0.0623 M$$

82. A sample of magnesium was burnt in air to give mixture of MgO and Mg<sub>3</sub>N<sub>2</sub>. The ash was dissolved in 60 meq. of HCl and the resulting solution back titrated with NaOH. 12 meq. of NaOH were required to reach the end point. An excess of NaOH was then added and the solution distilled. The ammonia released was then trapped in 10 meg. of second acid solution. Back titration of this acid solution required 6 meq. of the base. Calculate percentage magnesium burnt to the nitride. [Roorkee 1998]

[Hint: Let moles of Mg used for MgO and Mg<sub>3</sub>N<sub>2</sub> are x and y respectively.

$$2Mg + O_2 \longrightarrow 2MgO$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$
Moles of MgO =  $x$ , Moles of Mg<sub>3</sub>N<sub>2</sub> =  $y/3$ 
MgO + 2HCl  $\longrightarrow$  MgCl<sub>2</sub> + H<sub>2</sub>O
Mg<sub>3</sub>N<sub>2</sub> + 8HCl  $\longrightarrow$  3MgCl<sub>2</sub> + 2NH<sub>4</sub>Cl

Solution will contain x moles of MgCl<sub>2</sub> and 2y/3 moles of NH<sub>4</sub>Cl.

Moles of HCl used = 2x + 8y/3 for MgO and Mg<sub>3</sub>N<sub>2</sub>

$$2x + \frac{8y}{3} = 60 - 12 = 48$$
 ... (i)

Moles of NH<sub>4</sub>Cl formed = moles of NH<sub>3</sub>

= moles of HCl used to absorb NH<sub>3</sub>  

$$2y/3 = 4$$
  
 $y = 6$ 

From eq. (i) 
$$2x + \frac{8 \times 6}{3} = 48$$
$$x = 16$$

$$x = 16$$
  
% Mg used for Mg<sub>3</sub>N<sub>2</sub> =  $\left(\frac{6}{6+16}\right) \times 100 = 27.27\%$ 

**83.** A sample of hard water contains 96 ppm of  $SO_4^{2-}$  and 183 ppm of HCO<sub>3</sub>, with Ca<sup>2+</sup> as the only cation. How many moles of CaO will be required to remove HCO<sub>3</sub> from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual Ca<sup>2+</sup> ions? (Assume CaCO<sub>3</sub> to be completely insoluble in water). If the Ca<sup>2+</sup> ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH?

(One ppm means one part of the substance in one million parts of water.) [LLT. May 1997]

- **84.** Gastric juice contains 3 g of HCl per litre. If a person produces 2.5 litre of gastric juice per day, how many antacid tablets each containing 400 mL of Al(OH)<sub>3</sub> are needed to neutralize all the HCl produced in one day? [Dhanbad 1991]
- 85. Zinc can be determined volumetrically by the precipitation reactions.

$$3Zn^{2+} + 2K_4[Fe(CN)_6] \longrightarrow K_2Zn_3[Fe(CN)_6] + 6K^+$$

A sample of Zn ore weighing 1.5432 g was prepared for reaction and required 34.68 mL of 0.1043 M K<sub>4</sub>[Fe(CN)<sub>6</sub>] for titration. What is percentage of zinc in the ore?

- A mixture of KOH and Na<sub>2</sub>CO<sub>3</sub> solution required 15 mL of N/20 HCl using phenolphthalein as indicator. The same amount of alkali mixture when titrated using methyl orange as indicator required 25 mL of same acid, Calculate amount of KOH and Na<sub>2</sub>CO<sub>3</sub> present in solution.
- 87. 1000 mL O<sub>2</sub> at NTP was passed through Siemen's ozonizer so that the volume is reduced to 888 mL at same condition. Ozonized oxygen is passed through KI solution. Liberated  $I_2$  was titrated with 0.05 N hypo. Calculate volume of hypo used.
- 88. 1 g of an alloy of copper was dissolved in dilute H<sub>2</sub>SO<sub>4</sub> and solution made up to 1 litre. To 20 mL of this solution excess of KI was added, liberated iodine required 10 mL of a sodium thiosulphate solution for complete titration. In another experiment 2.45 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was dissolved in a litre. Excess of KI was added to 20 mL of this solution; liberated iodine required 50 mL stock of same Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. Calculate amount of copper in the alloy.

(Given, equivalent mass of hypo = 158; equivalent mass of  $K_2Cr_2O_7 = 49$ 

- 89. 30 mL of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> liberated iodine from KI solution when the iodine was titrated with hypo solution (N/20), the titre value was 45 mL. Find the concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in g per litre.
- Excess of KI and dil. H<sub>2</sub>SO<sub>4</sub> were mixed in 50 mL H<sub>2</sub>O<sub>2</sub>. The liberated I<sub>2</sub> required 20 mL of 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Find out the strength of H<sub>2</sub>O<sub>2</sub> in g/litre.
- 91. 0.32 g sample of KI (impure) was dissolved in 1.1 millimoles of K<sub>2</sub>CrO<sub>4</sub> and 25 mL of 5 N H<sub>2</sub>SO<sub>4</sub>. Iodine formed was expelled off by boiling and the solution is now mixed with excess of pure KI and I2 liberated again which on titration required 14 mL of 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Calculate % purity of original KI sample.

$$2CrO_4^{2-} + 2H^{+} \longrightarrow Cr_2O_7^{2-} + H_2O$$
  
 $Cr_2O_7^{2-} + 6I^{-} + 14H^{+} \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$ 

**92.** 6 g sample of  $(Fe_3O_4 + Fe_2O_3)$  mixture and an inert material was treated with excess of aqueous KI which reduces all Fe<sup>3+</sup> to Fe<sup>2+</sup> ion. The resulting solution was diluted to 50 mL. 10 mL of the diluted solution titrated with 5.5 mL of 1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to react with all iodine. The I<sub>2</sub> from another 25 mL sample was extracted after which the Fe<sup>2+</sup> was titrated with 3.2 mL of 1 M MnO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> solution. Calculate percentage of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> in the mixture.

[Hint: Reactions involved are:

- (1)  $Fe_3O_4 + 2KI + 4H_2SO_4 \longrightarrow 3FeSO_4 + K_2SO_4 + 4H_2O + I_2$
- (2)  $Fe_2O_3 + 2KI + 3H_2SO_4 \longrightarrow 2FeSO_4 + K_2SO_4 + 3H_2O + I_2$
- $I_2 + 2S_2O_3^{2-} \longrightarrow 2\Gamma + S_4O_6^{2-}$ (3)
- (4)  $MnO_4 + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2Ol^+$
- 93. 25 mŁ H<sub>2</sub>O<sub>2</sub> were added to excess of acidified solution of KI. The iodine so liberated required 20 mL of 0.1 N sodium

thiosulphate for titration. Calculate the strength in terms of normality, percentage and volume. [M.L.N.R. 1996]

- 94. Cl<sub>2</sub> gas can be produced in the lab by the reaction,  $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$ If a 6.13 g sample that is 96% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is allowed to react
  - with 320 mL of HCl solution having density 1.15 g/mL and containing 30% by mass of HCl, what mass of Cl<sub>2</sub> is generated?
- 95. What is the weight in grams of available O<sub>2</sub> per litre from a solution of H<sub>2</sub>O<sub>2</sub>. 10 mL of which when titrated with N/20 KMnO<sub>4</sub> solution required 25 mL for the reaction,

$$2KMnO_4 + 5H_2O_2 + 4H_2SO_4 \longrightarrow$$
  
 $5O_2 + 8H_2O + 2KHSO_4 + 2MnSO_4$ 

96. A quantity of KMnO<sub>4</sub> was boiled with HCl and the gas evolved was led into a solution of KI. When the reaction was complete, the I2 liberated was titrated with a solution of hypo containing 124 g of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O per litre. It was found that exactly 60 mL were required to decolourise the solution of I<sub>2</sub>. What weight of KMnO<sub>4</sub> was used?

- 97: 0.5 g of a sample of bleaching powder was suspended in water and excess K1 is added. On acidifying with dil. H<sub>2</sub>SO<sub>4</sub>, I<sub>2</sub> was liberated which required 50 mL of N/10 hypo (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O). Calculate percentage of available Cl<sub>2</sub> in bleaching powder.
- 98. 1.2 g of a sample of CaOCl<sub>2</sub> were suspended in water made upto 100 mL. 25 mL of this solution was treated with KI and the 1<sub>2</sub> liberated corresponded to 10 mL of N/25 hypo. Calculate percentage of Cl<sub>2</sub> available in CaOCl<sub>2</sub>.
- 99. 1.6 g of pyrolusite was treated with 60 mL of normal oxalic acid and some H2SO4. The oxalic acid left undecomposed was made upto 250 mL, 25 mL of this solution required 32 mL of 0.1 N potassium permanganate (KMnO<sub>4</sub>). Calculate the percentage of pure MnO<sub>2</sub> in pyrolusite.
- 100. A sample of pyrolusite weighing 0.5 g is distilled with conc. HCl. The evolved Cl<sub>2</sub> when passed through a solution of KI liberates sufficient I<sub>2</sub> to react with 125 mL of N/12.5 hypo (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O). Calculate the percentage of MnO<sub>2</sub> in pyrolusite.

### Auswers

#### **Answers:** Subjective Type Questions

- **9.** 0.2 N **10.** 10 litre · 11. 0.08 N **12.** 0.2 N 13. 45 g/L
- **14.** 49.0 **15.** 5.09 **16.** (i) 248 (ii) 27.83
  - 17. 70.4%
- **18.** 30% **19.** HCl = 42.69, H<sub>2</sub>SO<sub>4</sub> = 57.31
- 20. 91.54%
- **23.** 12.0 **21.** 0.1435 g 22.50.0 **24.** vol. of water = 225 mL
- **25.** vol. of A = 200 mL, vol. of B = 800 mL
- **26.**  $CaCO_3 = 48.78\%$ ,  $MgCO_3 = 51.22\%$
- **27.** 1.875 g **28.** N/5 **29.** 182.5 g **30.** 60 mL
- **31.** 53, 106 **32.**  $Na_2CO_3 = 84.8\%$  **33.** 1.605 g
- **34.** Na<sub>2</sub>CO<sub>3</sub> = 2.12 g/L, NaHCO<sub>3</sub> = 0.84 g/L
- **35.** NaCl = 33.75%, Na<sub>2</sub>CO<sub>3</sub> = 66.25%
- **36.** NaOH = 2.0 g/L, Na<sub>2</sub>CO<sub>3</sub> = 1.325 g/L
- **37.** 66% **38.** 0.6 N 39. 88.96% **40.** 1.338 g
- 41. contamination percentage 46.95% 42. 40 mL 43. 35.5%
- 44. 5.372 g/L 45. 91.25 g/L, 2.5 N, 400 mL
- 46. with phenolphthalein 50 mL; with methyl orange 60 mL
- 47. 3.528 g/L 48. 31.75% 49. 87.5%

- 50. NaCl 61.81%, KCl 38.19%
- 51, 96.31%
- **52.** 35.5%

- 53. C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O 54. 18.68%
- **55.** 55.26%
- 57. 75 mL

- 58. N/100, N/33.3 59. 63, 126 62. 150 mL
- 60. N/5 61. 82% **63.** 30.90 **65.** (a) 50 (b) 150 mL
  - **67.** 1.625 g
- **69.** 94.7% 70. 337 mL
- 71. % of  $N_2 = 10.74\%$ ; % of  $(NH_4)_2C_2O_4 = 47.6\%$
- 73. Eq. mass 53, Mol. mass 106 74. 81.25%
- 75. Na<sub>2</sub>CO<sub>3</sub> 82.8%, Na<sub>2</sub>SO<sub>4</sub> 17.2%
- **76.**  $Na_2CO_3 = 0.5962$ ,  $K_2CO_3 = 0.6038$
- **78.** %  $H_2O_2 = 85$ ; vol. of dry  $O_2 = 124.79$  mL **79.** 41.52%
- **83.** 40 ppm, pH = 2.6989 **84.** 14 **85.** 22.85
- **86.** Na<sub>2</sub>CO<sub>3</sub> 0.053 g, KOH 0.014 g **87.** 400 mL **88.** 0.635 g
- **89.** 3.675.g **90.** 0.68 g 91. 98.56%
- 92. 17.4% Fe<sub>3</sub>O<sub>4</sub>, 24.6% Fe<sub>2</sub>O<sub>3</sub> **93.** N = 0.08 V = 0.448
- **94.** 4.263 g **95.** 2 g **96.** 0.9486 g 97. 35.5% 98. 4.7%
- 99. 76.125% 100.87%

## ILLUSTRATIONS OF OBJECTIVE QUESTIONS



- 1. A 5 molar solution of H<sub>2</sub>SO<sub>4</sub> is diluted from 1 L to 10 L. What is the normality of the solution? [M.H.C.E.T. 2005]
  - (a) 0.25 N

(b) 1 N

(c) 2N

(d) 7N

Ans. (b)

|Hint:

 $N_1V_1$ 

Normality = Molarity × Basicity of acid

$$= 5 \times 2 = 10$$

(Before dilution) (After dilution)

$$10 \times 1 = N_2 \times 10$$

$$N_2 = 1 N_1$$

2. A solution contains  $1.2046 \times 10^{24}$  hydrochloric acid molecules in one dm<sup>3</sup> of the solution. The normality of the solution is:

[H.C.E.T. 2005]

(a) 6N

(b) 2 N

(c) 4 N

(d) 8 N

Ans. (b) | Hint: Number of moles of HCl dissolved in 1 litre

$$=\frac{1.2046\times10^{24}}{6.023\times10^{23}}=2$$

Molarity = 2 M٠.

Normality = Molarity × Basicity of acid

 $= 2 \times 1 = 2 N1$ 

3. What volume of NaOH solution (0.1 N) is added to 40 mL of NaOH(0.1N) which is neutralized by 50 mL of HCI (0.2 N)?

[P.M.T. (Punjab) 2005]

(a) 80 mL

(b) 60 mL

(c) 40 mL

(d) 90 mL

Ans. (b) |Hint:

 $N_1V_1$  (acid) =  $N_2V_2$  (base)

$$0.2 \times 50 = N_2 V_2$$
 (base)

$$0.2 \times 50 = 0.1 \times V_2$$

or 
$$V_2 = \frac{10}{0.1} = 100 \text{ mL}$$

Volume of solution added = 100 - 40 = 60 mL]

- 4. The normality of a mixture obtained by mixing 100 mL 0.2 M H<sub>2</sub>SO<sub>4</sub> and 100 mL 0.2 M NaOH is:
  - (a) 0.2 N

(b) 0.01 N

(c) 0.1 N

(d) 0.3 N

Ans. (c)

Hint:

Normality of  $H_2SO_4 = Molarity \times Basicity$  $= 0.2 \times 2 = 0.4$ 

Normality of  $NaOH = Molarity \times Acidity$ 

 $= 0.2 \times 1 = 0.2$ 

 $N_1V_1(H_2SO_4) - N_2V_2 \text{ (NaOH)} = N_{Resultant}(V_1 + V_2)$  $0.4 \times 100 - 0.2 \times 100 = N_{\text{Resultant}}(200)$ 

 $N_{\text{Resultant}} = 0.1 \text{ N}$ 

- 5. 35.4 mL of HCl is required for the neutralization of a solution containing 0.275 g of sodium hydroxide. The normality of hydrochloric acid is:
  - (a) 0.97 N

(b) 0.142 N

(c) 0.194 N

(d) 0.244 N

Ans. (c)

[**Hint :** Number of equivalents of NaOH =  $\frac{IVIADD}{Equivalent mass}$  $=\frac{0.275}{40}=6.875\times10^{-3}$ 

Number of equivalents of HCl = Number of equivalents of NaOH

$$\frac{NV}{1000} = 6.875 \times 10^{-3}$$
$$\frac{N \times 35.4}{1000} = 6.875 \times 10^{-3}$$
$$N = 0.1941$$

6. 15 volume sample of an H<sub>2</sub>O<sub>2</sub> solution is equivalent to:

(a) 5.30 N (b) 1.77 N

(c) 2.68 N

(d) 7.5 N

Ans. (c)

**Hint:** Volume strength of  $H_2O_2 = N \times 5.6$ 

$$15 = N \times 5.6$$

N = 2.681

7. KMnO<sub>4</sub> reacts with oxalic acid according to the equation,

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Here, 20 mL of 0.1 M KMnO<sub>4</sub> is equivalent to:

- (a)  $120 \text{ mL of } 0.25 M \text{ H}_2\text{C}_2\text{O}_4$  (b)  $150 \text{ mL of } 0.1 M \text{ H}_2\text{C}_2\text{O}_4$
- (c)  $50 \text{ mL of } 0.10 \text{ M H}_2\text{C}_2\text{O}_4$  (d)  $50 \text{ mL of } 0.20 \text{ M H}_2\text{C}_2\text{O}_4$ Ans. (c)

[**Hint**: 
$$\frac{M_1V_1}{n_1}$$
(MnO<sub>4</sub><sup>-</sup>) =  $\frac{M_2V_2}{n_2}$ (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>)  
For MnO<sub>4</sub><sup>-</sup>,  $\frac{M_1V_1}{n_1}$  =  $\frac{0.1 \times 20}{2}$  = 1  
For H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>,  $\frac{M_2V_2}{n_2}$  =  $\frac{50 \times 0.1}{5}$  = 1]

- **8.** 100 mL of *N*/5 NaOH will neutralize:
  - (a)  $0.06184 \text{ g of } H_3BO_3$
- (b)  $0.1855 \text{ g of } H_3BO_3$
- (c) 1.2368 g of H<sub>3</sub>BO<sub>3</sub>
- (d) 0.03092 g of H<sub>3</sub>BO<sub>3</sub>

Ans. (c)

**Hint:** Number of equivalents of  $H_3BO_3 = Number of equivalents$ 

$$= \frac{NV}{1000} = \frac{\frac{1}{5} \times 100}{1000} = 0.02 \qquad \dots (1)$$

Number of equivalents of  $H_3BO_3 = \frac{Praction}{Equivalent mass}$ 

$$\frac{1.2368}{62} = 0.0199 \approx 0.02$$
 ... (2)

9. What volume of 0.1 M H<sub>2</sub>SO<sub>4</sub> will be required to produce 17 g of H<sub>2</sub>S by the reaction,

$$5H_2SO_4 + 8Nal \longrightarrow 4Na_2SO_4 + 4I_2 + H_2S + 4H_2O$$
?

(a) 70 L

(b) 50 L

(c) 25 L

(d) 5L

Ans. (c)

|Hint: : 34 g H<sub>2</sub>S is formed by 5 mole of H<sub>2</sub>SO<sub>4</sub> :. 17 g H<sub>2</sub>S will be formed by 2.5 mole of H<sub>2</sub>SO<sub>4</sub>

Number of moles = 
$$\frac{MV}{1000}$$
  
2.5 =  $\frac{0.1 \times 1}{1000}$ 

or

$$V = 25000 \text{ mL} = 25 \text{ L}$$

**10.** 50 mL of a solution of Na<sub>2</sub>CO<sub>3</sub> neutralizes 49.35 mL of 4 *N* HCl. The reaction is represented as

$$CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O$$

The density of this  $Na_2CO_3$  solution is 1.25 g mL<sup>-1</sup>. The percentage of  $Na_2CO_3$  in it is:

(a) 47.7

(b) 37.7

(c) 26.7

(d) 16.7

Ans. (d)

$$\frac{M_1 V_1}{n_1} (\text{CO}_3^{2-}) = \frac{M_2 V_2}{n_2} (\text{H}^+)$$

[Hint:

 $n_1$  and  $n_2$  are corresponding coefficients in the balanced equation,

$$\frac{M_1 \times 50}{1} = \frac{4 \times 49.35}{2}$$

$$M_1 = 1.974$$

 $M = \frac{x \times d \times 10}{m}$ 

 $\frac{m_{B}}{m_{B}}$ Where, x = Percentage by mass of solute

d =Density of solution  $m_B =$ Molar mass of solution

$$1.974 = \frac{x \times 1.25 \times 10}{106}$$
$$x = 16.7$$

11. A 0.492 g of KH<sub>2</sub>PO<sub>4</sub> is titrated against a solution of 0.112 M NaOH. The volume of the base required to do this is 25.6 mL. The reaction involved is,

$$KH_2PO_4 + NaOH \longrightarrow NaKHPO_4 + H_2O$$

The percentage purity of KH<sub>2</sub>PO<sub>4</sub> is:

(a) 88.45

(b) 78.42

(c) 79.06

(d) 46.32

Ans. (c)

**Hint:** Number of moles of  $KH_2PO_4 = Number$  of moles of NaOH

$$= \frac{MV}{1000} = \frac{0.112 \times 25.6}{1000}$$

$$= 2.8672 \times 10^{-3}$$
Mass of KH<sub>2</sub>PO<sub>4</sub> = 2.8672 × 10<sup>-3</sup> × 136
$$= 0.389 \text{ g}$$

Percentage purity of  $KH_2PO_4 = \frac{0.389}{0.492} \times 100 \approx 79.06$ 

- 12. When 3.92 g L<sup>-1</sup> of sample of Mohr's salt reacts completely with 50 mL N/10 KMnO<sub>4</sub> solution. The percentage purity of the sample of Mohr's salt is:
  - (a) 50

(b) 70

(c) 37

(d) 40

Ans. (a)

[Hint:  $N_1V_1$ (Mohr's salt) =  $N_2V_2$ (KMnO<sub>4</sub>)

$$N_1 \times 1000 = 1/10 \times 50$$
  
 $N_1 = 0.005$ 

Strength of Mohr's salt [FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O]

$$= 0.005 \times 392 = 1.96 \text{ g}$$

Percentage purity of Mohr's salt sample =  $\frac{1.96}{3.92} \times 100$ = 50%1

- **13.** A solution of 10 mL of  $M/10 \, \text{FeSO}_4$  was titrated with KMnO<sub>4</sub> solution in acidic medium, the amount of KMnO<sub>4</sub> used will be:
  - (a) 10 mL of 0.5 M
- (b) 10 mL of 0.1 M
- (c) 5 mL of 0.1 M
- (d) 10 mL of 0.02 M

Ans. (d)

[Hint: The reaction involved is,

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

$$\frac{M_1V_1}{n_1}$$
 (KMnO<sub>4</sub>) =  $\frac{M_2V_2}{n_2}$  (FeSO<sub>4</sub>)

$$\frac{M_2V_2}{n_2}$$
 (FeSO<sub>4</sub>) =  $\frac{0.1 \times 10}{10}$  = 0.1

$$\frac{M_1V_1}{n_1}$$
 (KMnO<sub>4</sub>) =  $\frac{0.02 \times 10}{2}$  = 0.1 ]

- 14. An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is:
  - (a) 40 mL

- (b) 20 mL
- (c) 100 mL
- (d) 400 mL

**Ans**: (a)

[Hint: 
$$N_{\text{oxalic acid}} = \frac{w_B \times 1000}{E_B \times V}$$

$$= \frac{6.3 \times 1000}{63 \times 250} = 0.4$$

$$N_1V_1$$
 (oxalic acid) =  $N_2V_2$  (NaOH)

$$0.4\times 10=0.1\times V_2$$

$$V_2 = 40 \text{ mL}$$

- 15. The formula mass of an acid is 82 amu. In a titration, 100 cm<sup>3</sup> of a solution of this acid containing 39 g of the acid per litre was completely neutralized by 95 cm<sup>3</sup> of aqueous solution of NaOH containing 40 g NaOH per litre of solution. What is the basicity of the acid?
  - (a) 4

(b) 2

(c) 1

(d) 0

**Ans**: (b)

Hint:

$$N_{\text{NaOH}} = 1$$
 (: 40 g/litre = 1 N NaOH)  
 $N_1 V_1 (\text{acid}) = N_2 \dot{V}_2 (\text{NaOH})$ 

$$N_1 \times 100 = 1 \times 95$$

$$N_1 = 0.95$$

$$\mathbf{v}_1 = 0.93$$

$$N = \frac{w_B \times 1000}{E_B \times V}$$

$$0.95 = \frac{39 \times 1000}{E_B \times 1000}$$

$$E_{R} = 41$$

Equivalent mass =  $\frac{\text{Molecular mass}}{\text{Basicity}}$ 

$$41 = \frac{82}{\text{Basicity}}$$

# **OBJECTIVE QUESTIONS**



Note: Choose the correct answer(s) out of given alternatives for each question.

1.	A normal solution:		(a) equal to its mol. mass $\square$ (b) 1/3 of its mol. mass $\square$	J
	(a) contains one gram equivalent mass of the substance in		(c) $1/6$ of its mol. mass $\square$ (d) $1/5$ of its mol. mass $\square$	J
	one litre solution $\Box$	11.	In the reaction,	
	(b) contains one gram molecular mass of the substance in		$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$	
	one litre solution		equivalent mass of iodine is: [M.P. (P.M.T.) 2004	η
	(c) contains one gram equivalent mass of the substance in		(a) equal to its molecular mass	Ī
	100 mL of the solution		(b) 2/3 the molecular mass	]
^	(d) is that whose concentration is known		(c) 2/9 the molecular mass	]
2.	Which one of the following is a standard solution?		(d) twice the molecular mass	]_
	(a) it contains one gram equivalent mass of the substance	12.	A molal solution is one that contains one mole of the solut	e
	in one litre solution  (b) its strength is accurately known		in:	
			(a) 1000 g of the solvent	J
	()	1		]
	(d) a solution which has been prepared from pure substance			
2	The medianter mass of H DO is 92 Its assistant mass if		(d) 22.4 litre of the solvent	
3.	The molecular mass of H <sub>3</sub> PO <sub>3</sub> is 82. Its equivalent mass if	13.	In alkaline conditions, KMnO <sub>4</sub> reacts as follows,	
	it is completely neutralised, is:  (a) 82		$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$	
	(a) $62$		Therefore, its equivalent mass will be:	
4.	The molecular mass of Mohr's salt, $FeSO_4(NH_4)_2SO_4\cdot 6H_2O$ ,		(a) 31.6	٦
т.	is 392. Its equivalent mass is:			_
	(a) 196	14.		_
	(c) 98.0	- "	the best indicator to be used is:	-,
5.	$\operatorname{Cr}_2\operatorname{O}_7^{2-} \xrightarrow{\operatorname{H}^+} \operatorname{Cr}^{3+}$ equivalent mass of $\operatorname{Cr}_2\operatorname{O}_7^{2-}$ is:			
<i>J</i> ,				_
				_
	(a) $\frac{\text{mol. mass}}{3}$ $\square$ (b) $\frac{\text{mol. mass}}{6}$ $\square$		(-)	
	3	15.	For the preparation of a litre of $N/10$ solution of $H_2SO_4$ , w	/e
	(c) mol. mass $\square$ (d) $\frac{\text{mol. mass}}{4}$ $\square$		need:	*
6.	Amount of oxalic acid required to prepare 250 mL of N/10		4	]
	solution (Mol. mass of oxalic acid = 126) is:			
	(a) $1.5759 g$	16.	Molecular mass of a tribasic acid is M. Its equivalent mas	SS
	(c) $15.75  \text{g}$	1	will be:	
7.	Normality of 2% H <sub>2</sub> SO <sub>4</sub> solution by volume is nearly:		(a) $M/3$	
	(a) 2		(-)	
	(c) $0.2$ $\Box$ (d) $0.4$ $\Box$	17.	A solution containing Fe <sup>2+</sup> ions is titrated with KMnC	)4
8.	The equivalent mass of KMnO <sub>4</sub> in the following reaction is:		solution. Indicator used will be:	
	[J.E.E. (Orissa) 2010]		(a) phenolphthalein $\Box$ (b) methyl orange	
	$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$	İ	(-)	
	(a) $M/2$ $\Box$ (b) $M/3$ $\Box$	18.	If 200 mL of N/10 HCl were added to 1 g calcium carbonate	e,
	(c) $M/5$ $\square$ (d) $M/4$ $\square$		what would remain after the reaction?	
	[Hint: Change in oxidation number of Mn per molecule = $7 - 2$		(a) $CaCO_3$ $\Box$ (b) $HCl$	
	= 5,  Eq. mass = M/5]		(-)	
9.	When KMnO <sub>4</sub> is reduced with oxalic acid in acidic	19.	How many mL of 1 M H <sub>2</sub> SO <sub>4</sub> acid solution is required t	to
	medium, the oxidation number of Mn changes from:		neutralise 10 mL of 1 M NaOH?	
	(a) 7 to 4		(a) $5 \text{ mL}$	_
	(c) $7 \text{ to } 2$ $\square$ (d) $4 \text{ to } 2$ $\square$			
10.		20.	200 mL of 3 N HCl were mixed with 200 mL of 6 N H <sub>2</sub> SC	-
	$2BrO_3^- + 12H^+ + 10e \longrightarrow Br_2 + 6H_2O$		solution. The final normality of H <sub>2</sub> SO <sub>4</sub> in the resultan	nt
	the equivalent mass of sodium bromate is:	İ	solution will be:	

	(a) $9 N$ $\square$ (b) $3 N$		33.	In an experiment, 20 mL			
0.1	(c) $6N$ $\Box$ (d) $2N$					nal AgNO <sub>3</sub> solution. AgC	
21.	The volume of water to be added to 400 mL of N/8 HC	l to				of acid was titrated with	N/20
	make it exactly $N/12$ , is:			NaOH solution. The volu		•	
	(a) 400 mL			(a) 10 mL		(b) 20 mL	
22.	100 mL of 0.3 N HCl were mixed with 200 mL of 0.6 N H <sub>2</sub> :		24	(c) 30 mL		(d) 5mL	
22.	solution. The final normality of acid was:	304	34.	lodine solution is prepar			-
	(a) $0.4 N$ $\square$ (b) $0.5 N$			(a) NaOH (c) H <sub>2</sub> O		(b) Na <sub>2</sub> CO <sub>3</sub> (d) KI	
	(c) $0.6 N$		35	Which one of the follow			
23.	The molecular mass of NaOH is 40.50 mL of a solu			(a) oxalic acid		s not a primary standard: (b) sodium thiosulphate	
	containing 2 g of NaOH in 500 mL will require for comp			(c) sodium hydroxide		(d) potassium dichromat	
	neutralisation:		36.	Which one of the follow		• •	
	(a) 10 mL decinormal HCl			(a) KMnO <sub>4</sub>		(b) CuSO <sub>4</sub> -5H <sub>2</sub> O	
	(b) 20 mL decinormal HCl			(c) I <sub>2</sub>		(d) $H_2SO_4$	
	(c) 50 mL decinormal HCl		37.	When 10 mL of 10 M sol			1 M
	(d) 25 mL decinormal HCl			solution of NaOH are mi	xed,	the resulting solution will	be:
24.	50 g of a sample of NaOH required for complete neu			(a) acidic		(b) neutral	
	lisation, I litre N HCl. What is the percentage purity	/ of		(c) alkaline		(d) cannot be predicted	
	NaOH?		38.	1.0 g of a metal carbonat	e net	itralizes 200 mL of 0.1 N	HCI.
	(a) 80			The equivalent mass of t	he m	etal will be:	
	(c) 60 (d) 50		ľ	(a) 50	$\Box$	(b) 40	
25.	Weight of iodine required to oxidise 500 mL N Na <sub>2</sub> S	$_2O_3$		(c) 20		(d) 100	
	solution, is:		39.	The normality of a 26			nonia
	(a) $6.35  \text{g}$			(density 0.885 g/mL) is a	рргох	timately:	
24	(c) 127 g			(a) 1.5		(b) 4.0	
26.	25 mL N K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> acidified solution will liberate ioo	line		(c) 0.4		(d) 153	
	from KI solution:		40.	The molarity of pure wat			
	(a) $0.3175 g$			(a) 18 <i>M</i>		(b) 50.0 <i>M</i>	
27	(c) 31.75 g			(c) 55.6 M		(d) 100 M	
27.	The indicator used in iodometric titrations is:	,	41.	$5.0 \text{ g of } \text{H}_2\text{O}_2 \text{ is prese}$			
	(a) phonolphthalein				is 34	4. The molarity of the sol	ution
28.	(c) potassium iodide			is:	_	4 . 0 . 15	_
20.	Which of the following acids is added in the titration oxalic acid and potassium permanganate?	1 ()		(a) 1.5 M		(b) 0.15 <i>M</i>	Ļ
	(a) HNO <sub>3</sub>		40	(c) 3.0 <i>M</i>		(d) 50 M	
	(c) CH <sub>3</sub> COOH		42.	2 N solution of sodium cof strength:	агроі	nate is equivalent to a sol	ution
29.	In the titration of $K_2Cr_2O_7$ iodometrically, near the end p			(a) 106 g per 100 mL	П	(b) 52 a mar 100 ml	
	the colour of the solution becomes;	Ome	l	(c) 10.6 g per 100 mL		(b) 53 g per 100 mL (d) 5.3 g per 100 mL	
	(a) green		43	Which one of these solu			
	(c) yellow		"	(a) 8 g KOH per 100 mL		s ikis the trighest horman	ty:
30.	In the titration of ferrous ammonium sulphate and potass			(b) $0.5 M H_2 SO_4$			
	dichromate, the external indicator used is:			(c) 6 g of NaOH per 100	ml.	Ÿ.	
	(a) KCNS (b) NH <sub>4</sub> CNS			(d) $N H_3 PO_4$	,		
	(c) $K_3 Fe(CN)_6$ $\Box$ (d) $K_4 Fe(CN)_6$		44.	1 g of a metal required 50	mL	of 0.5 N HCl to dissolve it	
31.	0.1 N solution of a dibasic acid can be prepared by dissolu	/ing		equivalent mass of the n			
	0.45 g of the acid in water and diluting to 100 mL.	The		(a) 25		(b) 50	
	molecular mass of the acid is:			(c) 20		(d) 40	
	(a) 45		45.	What volume of CO <sub>2</sub> at N		•	ction
	(c) 135			of 100 mL of 0.2 N HCl			
32.	100 mL of 0.2 N HCl solution is added to 100 mL of			(a) 112 mL		(b) 224 mL	
	N AgNO <sub>3</sub> solution. The molarity of nitrate ions in	the		(c) 448 mL		(d) 120 mL	
	resulting mixture will be:		46.	The equivalent mass of	phos	phoric acid (H <sub>3</sub> PO <sub>4</sub> ) is 4	19. It
	(a) $0.05 M$			behaves as acid.		-	
	(c) $0.1 M$			(a) monobasic		(b) dibasic	
				(c) tribasic		(d) tetrabasic	

47.	The normality of 10% (mass/volume) acetic acid is:		(c) 1.5 litre of $N/2$ HCl and 0.5 litre of $N/10$ HCl
	(a) 1 N		(d) 0.7 litre of $N/2$ HCl and 1.3 litre of $N/10$ HCl
40	(c) 1.7 N	58.	The molar concentration of the chloride ion in the solution
48.	In the reaction of sodium thiosulphate with iodine in aqueous		obtained by mixing 300 mL of 3.0 M NaCl and 200 mL of 4.0
	medium, the equivalent mass of sodium thiosulphate is equal		M solution of BaCl <sub>2</sub> is:
	to: [J.E.E. (W.B.) 2010]		(a) 1.6 M
	(a) molar mass of sodium thiosulphate		(c) $5.0 M$ $\Box$ (d) $0.5 M$ $\Box$
	(b) the average of molar masses of $Na_2S_2O_3$ and $I_2$	59.	The normality of $0.3 M$ phosphorous acid ( $H_3PO_3$ ) is:
	(c) half the molar mass of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>		(a) 0.1
40	(d) twice the molar mass of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	(0)	(c) 0.3
49.	How many grams of CH <sub>3</sub> OH would have to be added to	60.	A 100 mL solution of 0.1 N HCl was titrated with 0.2 N NaOH
	water to prepare 150 mL of a solution that is 2.0 M CH <sub>3</sub> OH?	}	solution. The titration was discontinued after adding 30 mL
	(a) $9.6$		of NaOH solution. The titration was completed by adding
50			0.25 N KOH solution. The volume of KOH required for
50.	On dissolving 1 mole of each of the following acids in one	ļ	completing the titration is:
	litre water, the acid which does not give a solution of strength IN is:		(a) 70 mL
		61	(c) 35 mL
	(a) HCl $\Box$ (b) HClO <sub>4</sub> $\Box$ (c) HNO <sub>3</sub> $\Box$ (d) H <sub>3</sub> PO <sub>4</sub> $\Box$	61.	1 See and a see a
51	0.16 g of a dibasic acid required 25 mL of decinormal NaOH	1	upto 250 mL. The volume of 0.1 N NaOH required to
51.	solution for complete neutralisation. The molecular mass of		completely neutralise 10 mL of this solution is: [I.I.T. 2001]
	the acid is:		(a) 40 mL
	(a) 32	62.	
	(c) 128	()2.	In order to prepare one litre normal solution of KMnO <sub>4</sub> , how
52.	5 mL of N HCl, 20 mL of N/2 H <sub>2</sub> SO <sub>4</sub> and 30 mL of N/3		many grams of KMnO <sub>4</sub> are required if the solution is to
3 <b>2,</b>	HNO <sub>3</sub> are mixed together and volume made to one litre. The		be used in acid medium for oxidation? [P.E.T. (M.P.) 2002]— (a) 158 g
	normality of the resulting solution is:		, ,
	(a) N/5	63.	-
	(c) N/20	0.5.	3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. Equivalent weight of the metal
53.	The equivalent mass of MnSO <sub>4</sub> is half of its molecular mass		is: [K.C.E.T. 2002]
	when it is converted to:		(a) 33.25
	(a) $Mn_2O_3$ $\Box$ (b) $MnO_2$ $\Box$		(c) 12
	(c) $MnO_4^-$	64.	
54.	For the redox reaction,		(a) $HPO_4^{2-}$ $\square$ (b) $PO_4^{3-}$ $\square$
٠	$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$		(c) $H_2PO_4^-$
		65.	'a' g KHC <sub>2</sub> O <sub>4</sub> required to reduce 100 mL of 0.02 M KMnO <sub>4</sub>
	the correct coefficients of the reactants for the balanced		in acid medium and 'b' g KHC <sub>2</sub> O <sub>4</sub> neutralises 100 mL of 0.05
	reaction are:	I	M Ca(OH) <sub>2</sub> then:
	$MnO_4^ C_2O_4^{2-}$ $H^+$		(a) $a = b$
	(a) 2 5 16		(c) $a = 2b$
		66.	Which of the following statements is/are true about H <sub>3</sub> PO <sub>2</sub> ?
			(a) It is a tribasic acid
55.	(d) 2 16 5 $\square$ 100 mL solution consists 4 g caustic soda. The normality of		(b) One mole of it is neutralised by 0.5 mole of $Ca(OH)_2$
JJ.	the solution is:		(c) NaH <sub>2</sub> PO <sub>2</sub> is acidic salt
			(d) It disproportionates to $H_3PO_3$ and $PH_3$ on heating $\square$
	(a) 1.0	67.	Mixture of (1 mole BaF <sub>2</sub> ) and (2 mole H <sub>2</sub> SO <sub>4</sub> ) can be
56.	The amount of a caustic soda required for complete		neutralised by:
50.	neutralisation of 100 mL 0.1 N HCl is:		(a) 1 mole KOH $\Box$ (b) 2 mole Ca(OH) <sub>2</sub> $\Box$
	(a) 4.0 g		(c) 4 mole NaOH
	(c) $0.4  \mathrm{g}$	68.	$28 \text{ NO}_3^- + 3\text{As}_2\text{S}_3 + 4\text{H}_2\text{O} \rightarrow 6\text{AsO}_4^{3-} + 28\text{NO} + 9\text{SO}_4^{2-} + 8\text{H}^+.$
57	What volume of N/2 and N/10 HCl should be taken in order	1	What will be the equivalent mass of As <sub>2</sub> S <sub>3</sub> in above reaction?
~.·	to make a 2 litre solution of N/5 strength?		M. Wt M wt
	(a) 0.5 litre of N/2 HCl and 1.5 litre of N/10 HCl		2
	(b) 1 litre of N/2 HCl and 1 litre of N/10 HCl		(c) $\frac{M. \text{ wt.}}{24}$ $\square$ (d) $\frac{M. \text{ wt.}}{29}$ $\square$

	_		
69.	A solution of $Al_2(SO_4)_3$ ( $d = 1.253 \text{ g mL}^{-1}$ ) contains 22%	79.	20 mL of 0.5 N HCl when mixed with 35 mL of 0.1 N NaOH;
	salt by weight. The molarity, normality and molality of the	ĺ	the resulting solution will: [C.E.T. (Karnataka) 2005]
	solution are: [M.P. (P.M.T.) 2004]	1	(a) be neutral
	(a) $0.825 M$ , $48.3 N$ , $0.805 m$		(b) be basic
	(b) 0.805 <i>M</i> , 4.48 <i>N</i> , 0.825 <i>m</i>		(c) turn phenolphthalein solution pink
,	(c) $4.83  \text{M}, 4.83  \text{N}, 4.83  \text{m}$		(d) turn methyl orange red
		90	• •
70		80.	One mole of acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> on reaction with excess KI
70.	The equivalent mass of KIO <sub>3</sub> in the reaction,		will liberation moles of I <sub>2</sub> . [P.E.T. (Kerala) 2006]
	$2Cr(OH)_3 + OH^- + KIO_3 \longrightarrow 2CrO_4^{2-} + KI + 5H_2O$ is:		(a) 5
	[M.P. (P.E.T.) 2004]		(c) $3 \qquad \qquad \Box$ (d) $2 \qquad \qquad \Box$
	(a) molecular mass $\Box$ (b) molecular mass/3 $\Box$		[Hint: $K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3$
	(c) molecular mass/6 □ (d) molecular mass/2 □	1	$+ 7H_2O + 3I_2$
71.	The normality of mixture obtained by mixing 100 mL of 0.2 M	81.	The formula mass of Mohr's salt is 392. The iron present in
	$H_2SO_4 + 100 \text{ mL of } 0.2  M \text{ NaOH is:}$		it is oxidised by KMnO <sub>4</sub> in acid medium. The equivalent mass
	[C.E.C.E. (Bihar) 2004]		of Mohr's salt is: [C.E.T. (Karnataka) 2006]
PRESENT AL ANSWARE	(a) 0.2	ļ	(a) 392
	(c) $0.1$ $\Box$ (d) $0.3$ $\Box$		(c) 278
72.	A 25 mL solution of barium hydroxide on titration with a 0.1	82.	Which of the following concentration terms is/are indepen-
12.	· · · · · · · · · · · · · · · · · · ·	02.	•
	molar solution of hydrochloric acid gave a titre value of		dent of temperature?
	35 mL. The molarity of barium hydroxide solution was:		(a) Molarity
	[A.J.E.E.E. 2003]	1	(b) Molarity and mole fraction
	(a) 0.07 (b) 0.14		(c) Mole fraction and molality
	(c) $0.28$ $\Box$ (d) $0.35$ $\Box$	1	(d) Molality and normality
73.	Normality of 2 M sulphuric acid is: [C.B.S.E. 2003]	83.	Acidified KMnO <sub>4</sub> oxidises oxalic acid to CO <sub>2</sub> . What volume
	(a) $2N$ $\square$ (b) $4N$	1.	in litres of 10 <sup>-4</sup> M KMnO <sub>4</sub> required to completely oxidise 0.5
	(c) $0.5 N$		litres of $10^{-2}M$ oxalic acid in acid medium?
74.	A solution is formed by diluting 250 mL of 0.4 N H <sub>2</sub> SO <sub>4</sub> with		[E.A.M.C.E.T. (Medical) 2006]
	one litre of water. The normality of above formed solution is:		(a) 125
	[A.F.M.C. 2003]	1	(c) 200
	(a) $0.4 N$		[Hint: Normality of KMnO <sub>4</sub> = $5 \times 10^{-4} N$
	(c) $0.040 N$	1.	Normality of oxalic acid = $2 \times 10^{-2} N$
75.	35.4 mL of HCl is required for the neutralisation of solution	84.	The volume of water to be added to $100 \text{ cm}^3$ of $0.5 N \text{ H}_2\text{SO}_4$
	containing 0.275 g of sodium hydroxide. The normality of	1 "	to get decinormal concentration is: [C.P.M.T. 2006;
	hydrochloric acid is: [C.P.M.T. 2003]		BCECE 2008]
	(a) $0.97 N$		(a) $400  \text{cm}^3$
	(c) $0.194 N$ $\Box$ (d) $0.244 N$ $\Box$		(c) $500 \text{cm}^3$
76.	KI when mixed with CuSO <sub>4</sub> solution in iodometric titration,		[Hint: Let the $V \text{ cm}^3$ of water be added. Total volume becomes
	gives: [M.P. (P.M.T.) 2005]		
	(a) $CuI_2 + K_2SO_4$ $\Box$ (b) $Cu_2I_2 + K_2SO_4$ $\Box$		$(100 + V) \text{ cm}^3$ .
	(c) $K_2SO_4 + Cu_2I_2 + I_2$		$100 + V) \times 0.1 = 100 \times 0.5$
77.	The equivalent weight of phosphoric acid ( $H_3PO_4$ ) in the		or $V = \frac{100 \times 0.5}{0.1} - 100 = 400 \text{ cm}^3$
"		05	0.1
	reaction,	85.	Consider a titration of potassium dichromate solution with
	NaOH + $H_3PO_4 \longrightarrow NaH_2PO_4 + H_2O$ is:		acidified Mohr's salt solution using diphenylamine as
	[B.H.U. (Medical) 2005]		indicator. The number of moles of Mohr's salt required per
	(a) 59		mole of dichromate is: [I.I.T. 2007]
ano.	(c) 25		(a) 3
78.	The volumes of 4 N HCl and 10 N HCl required to make 1	0.	(c) 5
	litre of 6 N HCl are : [C.E.E. (Kerala) 2004]	86.	
	(a) 0.75 litre of 10 N HCl and 0.25 litre of 4 N HCl		$(Cr_2O_7^{2-})$ is reduced to $Cr^{3+}$ ion. The equivalent weight of
	(b) 0.25 litre of 10 N HCl and 0.75 litre of 4 N HCl		$K_2Cr_2O_7$ in this reaction is: [E.A.M.C.E.T. (Med.) 2007]
•	(c) 0.67 litre of 4 $N$ HCl and 0.33 litre of 10 $N$ HCl		(a) $\frac{\text{Mol. wt.}}{3}$ $\square$ (b) $\frac{\text{Mol. wt.}}{6}$ $\square$
	(d) $0.8$ litre of $4 N$ HCl and $0.20$ litre of $10 N$ HCl		9
	(e) 0.5 litre of 4 N HCl and 0.5 litre of 10 N HCl $\Box$		(c) $\frac{\text{Mol. wt.}}{\text{Mol. wt}}$

87.	For the reaction,		(mol. mass = 158) present in 250 mL of 0.04 $M$ KMnO <sub>4</sub>
	$Na_2CO_3 + 2HC1 \longrightarrow 2NaC1 + H_2O + CO_2$		solution? [C.P.M.T. 2008]
	The equivalent weight of Na <sub>2</sub> CO <sub>3</sub> is: [A.M.U. (Engg.) 2007]		(a) 0.02
	(a) $M/2$ $\square$ (b) $M$ $\square$		(c) 0.04
	(c) $2 M$ $\square$ (d) $M/4$ $\square$		
88.	For the reaction between KMnO <sub>4</sub> and H <sub>2</sub> O <sub>2</sub> , the number		[Hint: Eq. mass of $KMnO_4 = \frac{Mol. mass}{5}$
	of electrons transferred per mole of H <sub>2</sub> O <sub>2</sub> are:		Normality = $5 \times Molarity$
	[D.P.M.T. 2007]		$0.04 M \text{ KMnO}_4 \text{ soln.} = 0.2 N \text{ KMnO}_4 \text{ soln.}$
	(a) one $\Box$ (b) two $\Box$		No. of equivalents of KMnO <sub>4</sub> in 250 mL solution
	(c) three $\Box$ (d) four $\Box$		$=\frac{0.2}{4}=0.05$
89.	The equivalent mass of phosphoric acid (H <sub>3</sub> PO <sub>4</sub> ) in the	94.	The volumes of two HCl solutions $A(0.5 N)$ and $B(0.1 N)$ to
	reaction,		be mixed for preparing 2L of 0.2 N HCl solution are:
	$NaOH + H_3PO_4 \longrightarrow NaH_2PO_4 + H_2O$ is: [B.H.U. 2005]		[E.A.M.C.E.T. (Med.) 2008]
	(a) 59		(a) $0.5 \text{ L of } A + 1.5 \text{ L of } B$
	(c) 25		(b) $1.5 \text{ L of } A + 0.5 \text{ L of } B$
90.	The molality of 1L solution of 93% H <sub>2</sub> SO <sub>4</sub> (w/V) having		(c) $1 \operatorname{L} \text{ of } A + 1 \operatorname{L} \text{ of } B$
CHECKS SECURIC STATE	density 1.84 g/mL is: [B.V. (Pune) 2006]		(d) $0.75 \text{ L of } A + 1.25 \text{ L of } B$
	(a) 1.043 m		[ <b>Hint</b> : $x \times 0.5 + (2 - x) \times 0.1 = 2 \times 0.2$ ]
	(c) $10.43 \mathrm{m}$	95.	Excess of CO <sub>2</sub> is passed through 50 mL of 0.5M calcium
	[ <b>Hint :</b> Mass of 1L solution = $1000 \times 1.84 = 1840 \text{ g}$		hydroxide solution. After the completion of the reaction, the
	Mass of solvent = $(1840 - 930) = 910$ g		solution was evaporated to dryness. The solid calcium
	Molelity 9301000 10.42.1		carbonate was completely neutralised with 0.1N hydrochloric
	Molality = $\frac{930}{98} \times \frac{1000}{910} = 10.43$		acid. The volume of hydrochloric acid required is:
91.	Amount of oxalic acid present in solution can be determined		[C.E.T. (Karnataka) 2009]
	by its titration with KMnO <sub>4</sub> solution in the presence of	Ì	(a) $200 \mathrm{mL}$ $\square$ (b) $500 \mathrm{mL}$ $\square$
	H <sub>2</sub> SO <sub>4</sub> . The titration gives unsatisfactory result when carried		(c) $400 \mathrm{mL}$ $\square$ (d) $300 \mathrm{mL}$ $\square$
	out in the presence of HCl, because HCl: [A.I.E.E. 2008]		[ <b>Hint</b> : 50 mL 0.5 M Ca(OH) <sub>2</sub> = 50 mL 0.5 M CaCO <sub>3</sub>
	(a) oxidises oxalic acid to $CO_2$ and $H_2O$		$\equiv 50 \text{ mL } 1.0 \text{ N CaCO}_3$
	(b) gets oxidised by oxalic acid to chlorine □		$\equiv 500 \text{ mL } 0.1 \text{ N CaCO}_3$
	(c) furnishes H <sup>+</sup> ions in addition to those from oxalic acid		$\equiv 500 \text{ mL } 0.1 \text{ N HCl }]$
		96.	When a strong acid is titrated using a weak base, the pH at
	(d) reduces permanganate to Mn <sup>2+</sup>		the equivalence point is: [J.E.E. (Orissa) 2009]
	[Hint: $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$		(a) 7 $\square$ (b) > 7 $\square$
			(c) < 7
	$2MnO_4^- + 10HCl + 6H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O]$	97.	A solution containing Na <sub>2</sub> CO <sub>3</sub> and NaOH requires 300 mL of
92.	MnO <sub>4</sub> ions are reduced in acidic condition to Mn <sup>2+</sup> ions		0.1 N HCl using phenolphthalein as an indicator. Methyl
	whereas they are reduced in neutral condition to MnO <sub>2</sub> . The		orange is then added to above titrated solution when a
	oxidation of 25 mL of a solution X containing $Fe^{2+}$ ions		further 25 mL of 0.2 NHCl is required. The amount of NaOH
	required in acidic solution 20 mL of a solution Y containing		present in the original solution is: [J.E.E. (Orissa) 2009]
	$MnO_4^-$ ions. What volume of solution Y would be required		(a) $0.5 \mathrm{g}$ $\square$ (b) $1 \mathrm{g}$ $\square$
	to oxidise 25 mL of solution X containing $Fe^{2+}$ ions in neutral		(c) $2 g$ $\square$ (d) $4 g$ $\square$
	condition? [P.E.T. (Kerala) 2008]		<b>[Hint:</b> 25 mL 0.2 N HCl $\equiv$ 50 mL 0.1 N HCl. This is the acid
	(a) 11.4 mL	į.	required to neutralise 1/2 of Na <sub>2</sub> CO <sub>3</sub> present in solution.
	(c) 33.3 mL		Thus, the acid used for the neutralisation of NaOH in the
	[Hint: $\frac{5}{3} \times 20 = \frac{100}{3} = 33.3$ ]		solution = $(300 - 50)$ mL 0.1 N HCl solution
02			
93.			= 250 mL 0.1 N NaOH solution = $\frac{40}{10} \times \frac{250}{1000} = 1g$ ]
	into Mn <sup>2+</sup> . What is the number of equivalents of KMnO <sub>4</sub>		

Husu	vers _					,			
<b>1.</b> (a)	<b>2.</b> (b)	3. (c)	<b>4.</b> (d)	<b>5.</b> (b)	<b>6.</b> (a)	<b>7.</b> (d)	<b>8.</b> (c)	<b>9.</b> (c)	<b>10.</b> (d)
11. (a)	12. (a)	<b>13.</b> (d)	<b>14.</b> (c)	<b>15.</b> (b)	<b>16.</b> (a)	<b>17.</b> (d)	<b>18.</b> (c)	<b>19.</b> (a)	<b>20.</b> (b)
<b>21.</b> (c)	<b>22.</b> (b)	<b>23.</b> (c)	<b>24.</b> (a)	<b>25.</b> (b)	<b>26.</b> (b)	<b>27.</b> (d)	<b>28.</b> (d)	29. (a)	<b>30.</b> (c)
<b>31.</b> (b)	<b>32.</b> (c)	<b>33.</b> (a)	<b>34.</b> (d)	35. (c)	<b>36.</b> (b)	<b>37.</b> (a)	<b>38.</b> (a)	<b>39.</b> (d)	<b>40.</b> (c)
<b>41.</b> (a)	<b>42.</b> (c)	<b>43.</b> (c)	<b>44.</b> (d)	<b>45.</b> (b)	<b>46.</b> (b)	<b>47.</b> (c)	<b>48.</b> (a)	<b>49.</b> (a)	<b>50.</b> (d)
51. (c)	<b>52.</b> (d)	<b>53.</b> (b)	<b>54.</b> (a)	55. (a)	<b>56.</b> (c)	<b>57.</b> (a)	<b>58.</b> (c)	<b>59.</b> (d)	<b>60.</b> (d)
61. (a)	<b>62.</b> (b)	<b>63.</b> (a)	<b>64.</b> (a, b, c)	<b>65.</b> (b)	<b>66.</b> (b, d)	<b>67.</b> (b, c)	<b>68.</b> (d)	<b>69</b> ; (d)	<b>70.</b> (c)
71. (c)	<b>72.</b> (c)	<b>73.</b> (b)	<b>74.</b> (d)	<b>75.</b> (c)	<b>76.</b> (c)	<b>77.</b> (d)	<b>78.</b> (c)	<b>79.</b> (d)	<b>80.</b> (c)
<b>81.</b> (a)	<b>82.</b> (c)	<b>83.</b> (d)	<b>84.</b> (a)	<b>85.</b> (d)	<b>86.</b> (b)	<b>87.</b> (a)	<b>88.</b> (c)	<b>89.</b> (d)	<b>90.</b> (c)
<b>91.</b> (d)	<b>92.</b> (c)	<b>93.</b> (b)	<b>94.</b> (a)	<b>95.</b> (b)	<b>96.</b> (c)	<b>97.</b> (b)			



### Objective Questions for IIT ASPIRANTS



1. The value of n in the following equation is :

$$Cr_2O_7^{2-} + 14H^+ + ne^- \longrightarrow 2Cr^{3+} + 7H_2O$$

(a) 2

(b) 3

(c) 4

(d) 6

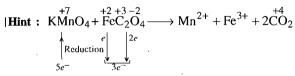
2. The number of moles of acidified  $KMnO_4$  required to oxidise one mole of ferrous oxalate,  $FeC_2O_4$  is :

(a) 5

(b) 3

(c) 0.6

(d) 1.5



5 mole  $FeC_2O_4 \equiv 3$  mole  $KMnO_4$ 

I mole  $FeC_2O_4 = 0.6$  mole  $KMnO_4$ 

- 3. A solution contains Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>. 10 mL of the solution required 2.5 mL of 0.1 *M* H<sub>2</sub>SO<sub>4</sub> for neutralization using phenolphthalein as indicator. Methyl orange is then added when a further 2.5 mL of 0.2 *M* H<sub>2</sub>SO<sub>4</sub> was required. Then amounts of Na<sub>2</sub>CO<sub>3</sub>-and NaHCO<sub>3</sub> in 1 litre of the solution are:
  - (a) 5.3 g and 4.2 g
- (b) 3.3 g and 6.2 g
- (c) 4.2 g and 5.3 g
- (d) 6.2 g and 3.3 g
- **4.**  $V_1$  mL of NaOH of normality x and  $V_2$  mL of Ba(OH)<sub>2</sub> of normality y are together sufficient to neutralize exactly, 100 mL of 0.1 N HCl. If  $V_1 : V_2 = 1 : 4$  and if x : y = 4 : 1, what fraction of the acid is neutralised by Ba(OH)<sub>2</sub>?
  - (a) 0.5

(b) 0.33

(c) 0.67

- (d) 0.25
- 5. A 0.518 g sample of limestone is dissolved in HCl and then the calcium is precipitated as  $CaC_2O_4$ . After filtering and washing the precipitate, it requires 40 mL of 0.25 N KMnO<sub>4</sub> solution acidified with  $H_2SO_4$  to titrate it as,

$$MnO_4^- + H^+ + C_2O_4^{2-} \longrightarrow CO_2 + Mn^{2+} + H_2O$$

The percentage of CaO in the sample is:

(a) 54%

(b) 27.1%

(c) 42%

(d) 84%

[**Hint :** Number of milliequivalents of CaC<sub>2</sub>O<sub>4</sub>, KMnO<sub>4</sub> and CaO will be same,

$$40 \times 0.25 = \frac{W56}{2} \times 1000$$
  
 $W = 0.28 \text{ g (Mass of CaO)}$   
% CaO =  $\frac{0.28}{0.518} \times 100 = 54\% \text{ J}$ 

**6.** When 40 mL of 0.1 N HCl and 20 mL of 0.1 M H<sub>2</sub>SO<sub>4</sub> are mixed together, the normality of mixture will be:

(a) 
$$\frac{1}{5}N$$

(b) 
$$\frac{2}{15}$$

(c) 
$$\frac{15}{2}$$

(d) 
$$\frac{5}{1}$$
  $\Lambda$ 

Hint:

$$N_1V_1 + N_2V_2 = N_R(V_1 + V_2)$$

$$0.1 \times 40 + 0.2 \times 20 = N_R \tag{60}$$

$$N_R = \frac{8}{60} = \frac{2}{15}$$

7. What is the normality of 0.3 M H<sub>3</sub>PO<sub>4</sub>, when it undergoes the reaction as:

$$H_3PO_4 + 2OH^- \longrightarrow HPO_3^{2-} + 2H_2O$$
?

(a) 0.3 *N* 

(b) 0.15 /V

(c) 0.60 N

(d) 0.90 N

8. In the mixture of (NaHCO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub>), volume of HCl required is x mL with phenolphthalein indicator and y mL with methyl orange indicator in same titration. Hence, volume of HCl for complete reaction of Na<sub>2</sub>CO<sub>3</sub> is:

(a) 2x

(b) y

(c) x/2

(d) (y-x)

|Hint: In presence of phenolphthalein, 50% Na<sub>2</sub>CO<sub>3</sub> is neutralised whereas NaHCO<sub>3</sub> remains unaffected. In presence of methyl orange, both Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> will be 100% neutralised.

Let volume of HCl for complete reaction of  $Na_2CO_3$ =  $V_1$  ml Volume of HCl for complete reaction of  $NaHCO_3$ 

=  $V_2$  mL With phenolphthalein, 50% Na<sub>2</sub>CO<sub>3</sub> will be neutralised

$$\therefore \qquad \frac{V_1}{2} = x \; , \qquad V_1 = 2x \; |$$

- 9. 40 mL of  $0.05 \, M \, \text{Na}_2 \, \text{CO}_3 \cdot \text{Na} \, \text{HCO}_3 \cdot 2 \, \text{H}_2 \, \text{O}$  (sesquicarbonate) is titrated against  $0.05 \, M \, \, \text{HCl}$ .  $x \, \, \text{mL}$  of HCl is used when phenolphthalein is the indicator and  $y \, \, \text{mL}$  HCl is used when methyl orange is the indicator in two separate titrations, hence (y x) is:
  - (a) 80 mL
- (b) 30 mL
- (c) 120 mL
- (d) none of these
- 10. Equivalent mass of  $H_3PO_2$  when it diproportionates into  $PH_3$  and  $H_3PO_3$  is (molecular mass = M):
  - (a) M

(b) M/2

(c) M/4

(d) 3M/4

[Hint:  $H_3^{+1}O_2 \longrightarrow H_3^{+2}O_3$   $E_{mass} = \frac{M}{2}$  (change in oxidation no. = 2)  $H_3^{+1}O_2 \longrightarrow PH_3$   $E_{mass} = \frac{M}{4}$ 

$$H_3PO_2 \longrightarrow PH_3$$
  $E_{ma}$  (change, in oxidation no. = 4)

The equivalent mass of  $H_3PO_2$  in the process of dispro-

portionation = 
$$\frac{M}{2} + \frac{M}{4} = \frac{3M}{4}$$
]

- 11. The reagent commonly used to determine hardness of water titrimetrically is:
  - (a) oxalic acid
- (b) disodium salt of EDTA
- (c) sodium citrate
- (d) sodium thiosulphate
- 12. The equivalent mass of sodium thiosulphate ( $Na_2S_2O_3 \cdot 5H_2O$ ) in the reaction,

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$
 is:

(a) 248

(b) 124

(c) 596

(d) 62

13. If 100 mL of the acid is neutralised by 100 mL of 4 M NaOH, the purity of conc. HCl (Sp. gravity = 1.2) is:

(a) 12%

(b) 98%

(c) 73%

(d) 43%

14.	2 moles of FeSO <sub>4</sub> are oxidised by x moles of KMnO <sub>4</sub> in acid
	medium into ferric sulphate, 3 moles of ferric oxalate are
	oxidised by y moles of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> in acid medium. The value
	of $(x/y)$ is:

(a) 6/5

(b) 2/15

(c) 18/5

(d) 3/5

15. What volume of  $0.05 M \text{ Cr}_2\text{O}_7^2$  in acid medium is needed for complete oxidation of 200 mL of  $0.6 M \text{ FeC}_2\text{O}_4$  solution?

(a) 0.6L

(b) 1.2L

(c) 2.4L

(d) 3.6L

16. KMnO<sub>4</sub> reacts with oxalic acid according to the reaction :  $2KMnO_4 + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$ 

Then, 20 mL of 0.1 M KMnO<sub>4</sub> is equivalent to:

(a)  $30 \text{ mL of } 0.5 \text{ M C}_2\text{H}_2\text{O}_4$  (oxalic acid)

(b)  $50 \text{ mL of } 0.1 \text{ M C}_2\text{H}_2\text{O}_4$  (oxalic acid)

(c)  $20 \text{ mL of } 0.5 M \text{ C}_2\text{H}_2\text{O}_4$  (oxalic acid)

(d) 10 mL of 0.1 MC<sub>2</sub>H<sub>2</sub>O<sub>4</sub> (oxalic acid)

[**Hint**: 
$$\frac{M_1V_1}{n_1}$$
(KMnO<sub>4</sub>) =  $\frac{M_2V_2}{n_2}$ (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>)  
$$\frac{0.1 \times 20}{2} = \frac{M_2V_2}{5}$$

 $M_2V_2 = 5$  {It is possible in case of (b)}]

17. Potassium permanganate is titrated against ferrous ammonium sulphate in acidic medium, the equivalent mass of potassium permanganate is:

(a)  $\frac{\text{molecular mass}}{2}$ 

(b) molecular mass

(c)  $\frac{\text{molecular mass}}{2}$ 

(d)  $\frac{\text{molecular mass}}{10}$ 

[Hint: The ionic reaction involved in titration is:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$
  
Since, a molecule of KMnO<sub>4</sub> accepts 5 electrons in acid medium, its equivalent mass will be  $\left(\frac{molecular\ mass}{5}\right)$ .]

**18.** Number of moles of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> that can be reduced by 1 mole of Sn<sup>2+</sup> ion, is:

(a) 1/3

(b) 3/2

(c) 5/6

(d) 6/5

[Hint: The redox reaction is:

$$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 3\text{Sn}^{2+} \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{Sn}^{4+}$$

∴ 1 mole of  $Sn^{2+}$  will reduce 1/3 mole of  $K_2Cr_2O_7$ .]

. 19. Potassium permanganate acts as an oxidising agent in acidic, alkaline as well as neutral media. Which among the following statements is incorrect?

- (a) N = M/5 (in acid medium)
- (b) N = M/3 (in alkaline medium)
- (c) N = M/3 (in neutral medium)
- (d) N = M (in alkaline medium)

20. The number of equivalents of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> required for the volumetric estimation of one equivalent of Cu<sup>2+</sup> is:

(a) 1/3

(b) 1

(c) 3/2

(d) 2/3

[Hint: Number of equivalents of reacting species in a chemical reaction are same.]

21. The equivalent mass of MnSO<sub>4</sub> becomes half of its molecular mass when it is converted into:

(a) MnO<sub>4</sub>

(b)  $MnO_2$  or  $Mn_3O_4$ 

(c)  $MnO_4^{2-}$ 

(d)  $Mn_2O_4^{2-}$ 

[Hint: When  $\stackrel{(+2)}{\text{MnSO}_4}$  is converted to  $\stackrel{(+4)}{\text{MnO}_2}$ , the oxidation number changes by 2, thus

Equivalent mass of MnSO<sub>4</sub> =  $\frac{\text{molecular mass}}{2}$ 

22. A solution of 10 mL of  $M/10 \text{ FeSO}_4$  was titrated with KMnO<sub>4</sub> solution in acidic medium, the amount of KMnO<sub>4</sub> used will be:

(a) 10 mL of 0.5 M

(b) 10 mL of 0.1 M

(c) 10 mL of 0.02 M

(d) 5 mL of 0.1 M

[Hint: The involved reaction is:

$$2KMnO4 + 8H2SO4 + 10FeSO4 \longrightarrow 5Fe2(SO4)3 + 2MnSO4 + K2SO4 + 8H2O$$

$$\frac{M_1V_1}{n_1}$$
 (KMnO<sub>4</sub>) =  $\frac{M_2V_2}{n_2}$  (FeSO<sub>4</sub>)

$$\frac{M_1V_1}{2} = \frac{0.1 \times 10}{10}$$

 $M_1V_1 = 0.2$  {Which is possible in (c)}]

23. Among the following reactions, used in titrations select the reaction(s) in which the chlorine is oxidised:

1.  $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$ 

2.  $H_2 + Cl_2 \longrightarrow 2HCl$ 

3.  $CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$ 

4.  $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$ 

(a) Reaction 2, 3, 4

(b) Reaction 1 only

(c) Reaction 1 and 3

(d) Reaction 4 only

(e) Reaction 2 and 4 only

24. Oxalic acid dihydrate, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O(s) is often used as a primary reagent to standardise sodium hydroxide solution. Which of these facts are reasons to choose this substance as a primary standard?

I. It is diprotic.

II. It is a stable compound that can be weighed directly in air.

III. It is available in pure form.

(a) III only

(b) I and II only

(c) II and III only

(d) I, II and III

25. A 20 mL sample of a Ba(OH)<sub>2</sub> solution is titrated with 0.245 M HCl. If 27.15 mL of HCl is required, what is the molarity of the Ba(OH)<sub>2</sub> solution?

(a) 0.166 M

(b) 0.180 M

(c) 0.333 M

(d) 0.666 M

**26.** A solution of which substance can best be used as both titrant and its own indicator in an oxidation-reduction titration?

(a) I<sub>2</sub>

(b) NaOCl

(c) K2Cr2O7

(d) KMnO<sub>4</sub>

27. A 0.2 g sample of benzoic acid, C<sub>6</sub>H<sub>5</sub>COOH is titrated with a 0.120 M Ba(OH)<sub>2</sub> solution. What volume of the Ba(OH)<sub>2</sub> solution is required to reach the equivalence point?

#### Substance

#### Molar mass

#### C<sub>6</sub>H<sub>5</sub>COOH

 $122.1 \text{ g mol}^{-1}$ 

- (a) 6.82 mL
- (b) 13.6 mL
- (c) 17.6 mL
- (d) 35.2 mL
- 28. What mass of magnesium hydroxide is required to neutralise 125 mL of 0.136 M HCl solution?

### Substance

#### Molar mass

 $Mg(OH)_2$ 

- $58.33 \text{ g mol}^{-1}$
- (a) 0.248 g
- (b) 0.496 g
- (c) 0.992 g
- (d) 1.98 g

29. In alkaline medium KMnO<sub>4</sub> reacts as follows,

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

Hence, its equivalent mass is:

(a) 31.6

(b) 63.2

(c) 126.4

- (d) 158
- 30. When 20 mL of M/10 NaOH are added to 10 mL of M/10 HCl, the resulting solution will:
  - (a) turn blue litmus red
  - (b) turn phenolphthalein solution pink
  - (c) turn methyl orange red
  - (d) will have no effect on either red or blue litmus

### tuswers

- 1. (d) 2. (c)
- **3.** (a)
- **4.** (a)
- 5. (a)
- **6.** (b)
- 7. (c)
- 8. (a)
- 9. (a)
- **10.** (d)
- 11. (b)
- 12. (a) 24. (c).

- 13. (a)
- 14. (b)
- 15. (b)
- 16. (b)
- 17. (b)
- 18. (a) 19. (b)
- 20. (b)
- 21. (b)
- 22. (c)
- 23. (c)

- 25. (a)
- 26. (d)
- 27. (a)
- 28. (b)
- 29. (d)

### **30.** (b)

# Matrix Matching Questions for IIT Aspirants

1. Match Column-I with Column-II:

#### Column-I (Acid)

#### Column-II

(Information)

- (a) CH3COOH
- (p) Tribasic  $\left(E = \frac{\text{Mol. mass}}{3}\right)$
- (b) H<sub>3</sub>PO<sub>4</sub>
- (q) Dibasic reducing
- (c) H<sub>2</sub>SO<sub>4</sub>
- (r) Dibasic  $\left(E = \frac{\text{Mol. mass}}{2}\right)$
- (d) H<sub>3</sub>PO<sub>3</sub>

(s) Monobasic (E = Mol. mass)

#### 2. Match Column-I with Column-II:

#### Column-I (Reaction)

(Equivalent mass of reactant)

Column-II

- (a)  $NH_3 \longrightarrow NO_3^-$
- Mol. mass
- (b)  $Fe_2S_3 \longrightarrow FeSO_4 + SO_2$
- (c)  $CaCO_3 + 2HCl \longrightarrow$
- Mol. mass
- $CaCl_2 + H_2O + CO_2$ (d)  $CuS \longrightarrow CuSO_4$
- (s) 50

### tuswers

- (a-s)
- (b-p)
- (c-r)
- (d-q, r) (d-r)

- 2. (a-r)
- (b-p)
- (c-q, s)

# **Assertion-Reason Type Questions**

The questions given below consist of an Assertion (A) and **Reason** (R). Use the following keys to choose the appropriate answer:

- (a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
- (c) If (A) is correct but (R) is incorrect.
- (d) If (A) is incorrect but (R) is correct.
- 1. (A) Equivalent mass of  $H_3PO_2$  is equal to its molecular mass.
  - (R) H<sub>3</sub>PO<sub>2</sub> is a monobasic acid.
- 2. (A) When Na<sub>2</sub>CO<sub>3</sub> is titrated against HCl in presence of phenolphthalein indicator, it is converted into NaCl.

- (R) Phenolphthalein shows colour change in the pH range of 3.5 to 4.6.
- 3. (A) 1 mole of H<sub>2</sub>SO<sub>4</sub> is neutralised by 2 moles of NaOH. However, 1 equivalent mass of H<sub>2</sub>SO<sub>4</sub> is neutralised by 1 equivalent of NaOH.
  - (R) Equivalent mass of H<sub>2</sub>SO<sub>4</sub> is half of its molecular mass and the equivalent mass of NaOH is equal to its molecular mass.
- 4. (A) Equivalent mass of KMnO<sub>4</sub> is equal to one-fifth of its molecular mass when it acts as an oxidising agent in acidic medium.
  - (R) Oxidation number of Mn in KMnO<sub>4</sub> is +7.

- **5.** (A) In the reaction,  $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$ ,  $I_2$  is
  - (R) During oxidation, loss of electron or electrons occur.
- (A) 5 M NaOH solution is diluted 10 times, its molarity becomes 50.
- (R) On dilution, molarity of the solution decreases.
- 7. (A) Iodimetric titrations are redox titrations.
  - (R) The iodine solution acts as an oxidising agent.
- 8. (A) H<sub>3</sub>BO<sub>3</sub> is a monobasic acid.
  - (R) H<sub>3</sub>BO<sub>3</sub> has one ionisable hydrogen atom.

#### tuswers

1. (a)

2. (c) 3. (b) 4. (b)

5. (d)

**6.** (d)

7. (a)

8. (c)

## THOUGHT TYPE QUESTIONS

#### **THOUGHT 1**

Pyrolusite, MnO<sub>2</sub>, is the main ore from which manganese is produced. The manganese content of the ore may be determined by reducing the MnO<sub>2</sub> under acidic conditions to Mn<sup>2+</sup> with the oxalate ion,  $C_2O_4^{2-}$ , the oxalate ion being oxidised to carbon dioxide during the reaction. The analytical determination is carried out by adding a known excess volume of oxalate solution to a suspension of the pyrolusite and digesting the mixture on a hot waterbath until all the MnO<sub>2</sub> has been reduced. The excess, unreacted oxalate solution is then titrated with standardized potassium permanganate, KMnO<sub>4</sub> solution after which the manganese content of the ore can be calculated.

A student prepared a standard solution of sodium oxalate by weighing 3.2 g of the dry anhydrous salt, dissolving it in distilled water and making the solution upto 500 mL. 25 mL of the oxalate solution required 24.76 mL of KMnO<sub>4</sub> solution.

- 1. What is the equivalent mass of MnO<sub>2</sub> in the present titration?
  - (a)  $M_{\text{mass}}/1$
- (b)  $M_{\text{mass}}/2$
- (c) M.mass/3
- (d)  $2M._{mass}/3$
- How many moles of  $C_2O_4^{2-}$  ions will be oxidised by 1 mole  $MnO_4^-$ ?
  - (a) 1/2

(b) 3/2

(c) 5/2

- (d) 7/2
- 3. Molarity of the sodium oxalate solution is .......
  - (a) 0.04776
- (b) 0.07446
- (c) 0.06447
- (d) 0.07644
- What is the molarity of KMnO<sub>4</sub> solution?
  - (a) 0.04776
- (b) 0.01929

(c) 0.038

- (d) 0.028
- 5. Role of KMnO<sub>4</sub> in the given titration can be described as:
  - (a) oxidising agent
  - (b) reducing agent
  - (c) indicator
  - (d) oxidising agent and indicator

### THOUGHT 2

For a series of indicators, the following colours and pH range over which colour change takes place are as follows:

Indicator	Colour change over pH range		
U	Yellow to blue	(pH 0.0 to 1.6)	
V	Red to yellow	(pH 2.8 to 4.1)	
	Red to yellow	(pH 4.2 to 5.8)	
X	Yellow to blue	(pH 6 to 7.7)	
$Y_{\cdot}$	Colourless to red	(pH 8.2 to 10)	

#### Choose the correct option:

- Indicator V could be used to find the equivalence point for 0.1 M acetic acid and 0.1 M ammonium hydroxide solution.
  - (a) True

- (b) False
- 2. Indicator Y could be used to distinguish between the solutions of ammonium chloride and sodium acetate.

- (b) False
- Indicator X could be used to distinguish between the solutions of ammonium chloride and sodium acetate.

- (b) False
- Indicator W would be suitable for use in the determination of the concentration of acetic acid in white vineger by base titration.
  - (a) True

- (b) False
- 5. Indicator U could be used to distinguish between 0.1 M and 0.01 M solution of sulphuric acid.
  - (a) True

### THOUGHT 3

Chemists work with standardized solution, a solution whose concentration is known. The requirements to standardize the solution are:

- 1. the volume of the solution
- 2. the number of moles of solute in that volume

A primary standard solution is used in determining the molarity of a solution. To find the molarity of HCl, 0.317 g of Na<sub>2</sub>CO<sub>3</sub>, the primary standard dissolved in water is used in titrating the solution of HCl. 22.9 mL of acid are required to neutralise the sodium carbonate. This is the needed volume (first requirement). The stoichiometric equation is used to know the second requirement.

 $2HCl(aq.) + Na_2CO_3(aq.) \longrightarrow 2NaCl + H_2O + CO_2 \uparrow$ 

- 1. What is the molarity of HCl in the above case?
  - (a) 0.261 M
- (b) 0.522 *M*

(c) 0.1 M

- (d) 1 M
- Equivalent mass of Na<sub>2</sub>CO<sub>3</sub> in the above equation will be :
  - (a) 106

(b) 53

(c) 26.5

(d) 13.25

3. The suitable indicator in the above titration will be:

- (a) phenolphthalein
- (b) methyl orange

(c) litmus

- (d) bromothymol blue
- 4. Solution of Na<sub>2</sub>CO<sub>3</sub> in water will be:
  - (a) acidic

(b) neutral

(c) basic

- (d) it can not be predicted
- 5. What fraction of Na<sub>2</sub>CO<sub>3</sub> will be neutralized by HCl in presence of phenolphthalein indicator?
  - (a) 1/3

(b) 2/3

(c) 1/2

(d) 1/4

#### **THOUGHT 4**

0.5 g bleaching powder was suspended in water and excess KI is added. On acidifying with dil.  $H_2SO_4$ ,  $I_2$  was liberated which required 50 mL of N/10 hypo( $Na_2S_2O_3\cdot 5H_2O$ ) in presence of starch. The reactions involved are :

I. 
$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2CHCl_2$$

II. 
$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

- III.  $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$
- 1. In the reaction (I), which one is reduced?
  - (a) CaOCl<sub>2</sub>
- (b) H<sub>2</sub>SO<sub>4</sub>

(c) Both

- (d) None
- 2. In the given titration, starch acts as:
  - (a) oxidising agent
- (b) indicator
- (c) reducing agent
- (d) catalyst
- 3. In reaction (II), Cl<sub>2</sub> acts as:
  - (a) reducing agent
  - (b) oxidising agent
  - (c) indicator
  - (d) both oxidising agent and indicator
- 4. Percentage of available chlorine in bleaching powder is:
  - (a) 35.5%

- (b) 71%
- (c) 17.25%
- (d) 50%
- 5. Starch forms iodo-starch complex in the given titration. The colour of the complex will be:
  - (a) green

- (b) blue
- (c) pale yellow
- (d) milky white

### Answer

Thought 1	<b>1.</b> (b)	<b>2.</b> (c)	<b>3.</b> (a)	<b>4.</b> (b)	5. (d)
Thought 2	<b>1.</b> (b)	<b>2.</b> (b)	<b>3.</b> (a)	<b>4.</b> (b)	<b>5.</b> (b)
Thought 3	<b>1.</b> (a)	<b>2.</b> (b)	<b>3.</b> (b)	<b>4.</b> (c)	<b>5.</b> (c)
Thought 4	<b>1.</b> (d)	<b>2.</b> (b)	<b>3.</b> (b)	<b>4.</b> (a)	<b>5.</b> (b)

### INTEGER ANSWER Type Questions

The answer to each of the following questions is a single digit integer, ranging from 0 to 9.

- 1. An aqueous solution of 0.63 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is:
- 2. In the standardisation of  $Na_2S_2O_3$  using  $K_2Cr_2O_7$  by iodometry, the equivalent mass of  $K_2Cr_2O_7$  is M/x. What is the value of x if M is the molecular mass of  $K_2Cr_2O_7$ ?
- 3. A sample of MnO<sub>2</sub> having percentage purity 13.05 is treated with HCl, liberating chlorine which is passed into KI solution.

- 30 mL of 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> are required to titrate the liberated iodine. What was the mass of MnO<sub>2</sub> sample taken?
- **4.** A solution is formed by diluting 250 mL 4 N H<sub>2</sub>SO<sub>4</sub> with 750 mL of water. The normality of the diluted solution is:
- **5.** 100 mL solution consists 8 g of NaOH. The normality of the solution is :
- **6.** If 300 mL of 3 N HCl is mixed with 300 mL of 6 N  $H_2SO_4$ . The final normality of the  $H_2SO_4$  in the resultant solution is:

#### Answers

1. (4) Eq. mass of oxalic acid dihydrate  $=\frac{126}{2}=63$ 

Normality of solution  $= \frac{4 \times 0.63}{63} = 0.04 \text{ N}$  $10 \times 0.04 = V \times 0.1 \qquad i.e., V = 4 \text{ mL}$ 

2. (6)  $K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$ 

Change in oxidation state of Cr per molecule = 12 - 6 = 6Thus, Eq. mass of  $K_2Cr_2O_7 = M/6$ i.e., x = 6

3. (1) 30 mL 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  $\equiv$  30 mL 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  $\equiv$  30 mL 0.1 N Cl<sub>2</sub>  $\equiv$  30 mL 0.1 N MnO<sub>2</sub>

Amount of MnO<sub>2</sub> =  $\frac{87}{2} \times \frac{0.1 \times 30}{1000} = 0.1305 \text{ g}$ Mass of sample =  $\frac{100}{13.05} \times 0.1305 = 1$ 

4. (1) Total volume of diluted solution = 1000 mL

Normality 
$$=\frac{250\times4}{1000}=1$$

- 5. (2) Normality  $=\frac{8}{40} \times \frac{1000}{100} = 2$
- 6. (3) Total volume becomes = 600 mL

Normality 
$$=\frac{300\times6}{600}=3 \text{ N}$$

# CHAPTER 18

# Qualitative Inorganic Analysis

#### Contents:

- 18.1 Introduction
- 18.2 Identification of Acidic Radicals
- **18.3** Identification of Acidic Radicals with Sodium Carbonate Extract
- 18.4 Identification of Basic Radicals
- **18.5** Chemical Reactions Involved in the Tests of Basic Radicals
- **18.6** Dry Tests

#### 18.1 INTRODUCTION

Qualitative inorganic analysis deals with the identification of radicals (cations and anions) in an inorganic salt or in a mixture of salts. A salt consists of two parts known as radicals. The positively charged part of a salt (cation) which has been derived from a base is termed **basic radical** and the negatively charged part of the salt (anion) which has been derived from an acid is termed **acidic radical**. For example, the salt copper sulphate is obtained by the action of a base (copper hydroxide) and an acid (sulphuric acid). Thus, it has copper ion ( $Cu^{2+}$ ) as a basic radical and sulphate ion ( $SO_4^{2-}$ ) as the acidic radical.

$$\begin{array}{cccc} Cu(OH)_2 \, + \, H_2SO_4 & \longrightarrow CuSO_4 \, + \, H_2O \\ & & Salt \\ & & & Cu^{2^+} & SO_4^{2^-} \\ & & & & Basic\ radical & Acidic\ radical \end{array}$$

A mixture may have two or more salts; thus qualitative inorganic analysis consists in identifying the presence of various cations and anions in it.

#### 18.2 IDENTIFICATION OF ACIDIC RADICALS

Most of these salts are acted upon by dilute  $H_2SO_4$  or dilute HCl and concentrated  $H_2SO_4$ . In each case, a gas is liberated which is characteristic of the particular acidic radical. There are some acidic radicals which are not decomposed either by dilute  $H_2SO_4$  or concentrated  $H_2SO_4$ . Hence, for the identification of the acidic radicals, the following scheme is followed:

- **Group I:** This group consists of radicals which are detected by dilute  $H_2SO_4$  or dilute HCl. These are (i) carbonate, (ii) sulphite, (iii) sulphide, (iv) nitrite and (v) acetate.
- **Group II:** This group consists of radicals which are detected by concentrated  $H_2SO_4$ . These are (i) chloride, (ii) bromide, (iii) iodide, (iv) nitrate and (v) oxalate.
- **Group III:** The radicals which do not give any characteristic gas with dilute and concentrated  $H_2SO_4$ . These are (i) sulphate, (ii) phosphate, (iii) borate and (iv) fluoride.

#### **GROUP I**

Take 0.2 g of the substance in a test tube and add 2 mL of dilute HCl or dilute  $H_2SO_4$ . Observe the reaction in cold, warm gently the contents and infer as follows:

S.No.	Observation	Inference	Confirmatory tests
1.	Brisk effervescence	CO <sub>3</sub> <sup>2-</sup>	Pass the gas in a test tube
	in cold with evolution	(Carbonate)	containing small quantity
	of colourless and odo-		of lime water. It turns
	urless gas.		milky.
2.	A colourless gas with	SO <sub>3</sub> <sup>2-</sup>	Moisten a piece of filter
	suffocating odour	(Sulphite)	paper with acidified
	having smell of		potassium dichromate and
	burning sulphur.	Į	put it on the mouth of the
			test tube. It turns green.
3.	A colourless gas with	S <sup>2</sup>	Moisten a piece of filter
	smell of rotten eggs.	(Sulphide)	paper with lead acetate
			solution and place it on
		1.	the mouth of the test
			tube. It turns black.
4.	A light brown gas.	NO <sub>2</sub>	(a) Pass the evolved gas
		(Nitrite)	through ferrous
			sulphate solution. It
			turns brown.
		}	(b) Mix the given salt or
	· · · · · · · · · · · · · · · · · · ·		mixture with a little of
		1	KI and add dilute
			H <sub>2</sub> SO <sub>4</sub> . Evolution of
			violet vapours.
			(c) Place the piece of
			filter paper on the
			mouth of test tube
		}	moistened with solu-
			tions of starch, pota-
			ssium iodide and ace-
_		GII GOOT	tic acid. It turns blue.
5.	Colourless vapours	CH <sub>3</sub> COO	(a) To the aqueous solu-
	with smell of vinegar.	(Acetate)	tion of substance add
		} · ' ·	neutral FeCl <sub>3</sub> solution
			→ blood red colour.
			(b) Rub the moistened
			salt or mixture with
			dry oxalic acid →
			smell of vinegar.

#### Reactions with explanations

(i) Carbonate: The carbonates are decomposed with dilute HCl or dilute  $H_2SO_4$  with the evolution of carbon dioxide gas. When this gas is passed through lime water, the lime water turns milky with the formation of calcium carbonate.

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
  
 $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$   
Lime water White ppt.

However, if the CO<sub>2</sub> gas is passed in excess, the milky solution becomes colourless due to the formation of soluble calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$
.  
White ppt. Soluble

**Note:** (a) Carbonates of bismuth and barium are not easily decomposed by dilute H<sub>2</sub>SO<sub>4</sub>. Dilute HCl should be used.

(b) Sulphur dioxide evolved from sulphites also turns lime water milky. In the test of carbonates, the evolved gas must be colourless and odourless (SO<sub>2</sub> is a pungent gas).

$$\begin{array}{c} \text{Ca(OH)}_2 + \text{SO}_2 & \longrightarrow \text{CaSO}_3 + \text{H}_2\text{O} \\ & \text{White ppt.} \end{array}$$

- (c) PbCO<sub>3</sub> reacts with HCl or H<sub>2</sub>SO<sub>4</sub> to give, in the initial stage, some effervescence but the reaction slows down due to formation of a protective insoluble layer of PbCl<sub>2</sub> or PbSO<sub>4</sub> on the surface of remaining salt or mixture.
- (ii) Sulphite: A sulphite with dilute H<sub>2</sub>SO<sub>4</sub> gives out sulphur dioxide gas which possesses suffocating smell of burning sulphur. When acidified potassium dichromate paper is exposed to the gas it attains green colour due to the formation of chromic sulphate.

$$\begin{array}{c} Na_2SO_3 \,+\, H_2SO_4 \longrightarrow Na_2SO_4 \,+\, H_2O \,+\, SO_2 \\ K_2Cr_2O_7 \,+\, H_2SO_4 \,+\, 3SO_2 \longrightarrow K_2SO_4 \,+\, Cr_2(SO_4)_3 + H_2O \end{array}$$

(iii) Sulphide: Dilute  $H_2SO_4$  decomposes a sulphide salt to form  $H_2S$  gas which smells like rotten eggs.

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$$

On exposure to this gas, the lead acetate paper turns black due to the formation of lead sulphide.

$$Pb(CH_3COO)_2 + H_2S \longrightarrow PbS + 2CH_3COOH$$
  
Black ppt.

Note: Sulphides of lead, cadmium, nickel, cobalt, antimony and stannic are not decomposed with dilute H<sub>2</sub>SO<sub>4</sub>. Conc. HCl should be used for their test. In such cases, however, brisk evolution of H<sub>2</sub>S takes place even by use of dilute H<sub>2</sub>SO<sub>4</sub> if a pinch of zinc dust is added.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$
  
 $HgS + 2H \longrightarrow Hg + H_2S$ 

(iv) Nitrite: When a nitrite is treated with dilute H<sub>2</sub>SO<sub>4</sub>, it yields a colourless nitric oxide gas which in contact with oxygen of the air becomes brown due to the formation of nitrogen dioxide.

$$\begin{array}{c} 2\text{NaNO}_2 + \text{H}_2\text{SO}_4 & \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HNO}_2 \\ & \text{Nitrous acid} \\ 3\text{HNO}_2 & \longrightarrow \text{H}_2\text{O} + 2\text{NO} + \text{HNO}_3 \\ 2\text{NO} + \text{O}_2 & \longrightarrow \text{2NO}_2 \\ & \text{Brown coloured gas} \end{array}$$

(a) On passing the gas in dilute FeSO<sub>4</sub> solution, brown coloured complex salt is formed.

$$FeSO_4 \cdot 7H_2O + NO \longrightarrow [Fe(H_2O)_5NO] \cdot SO_4 + 2H_2O$$
Brown coloured

(b) When a mixture of iodide and nitrite is acted upon by dilute H<sub>2</sub>SO<sub>4</sub>, the iodide is decomposed giving violet vapours of iodine.

(c) Starch-iodide paper is turned blue due to the liberation of iodine from iodide by nitrous acid which gives blue colour with starch.

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$$
 
$$2KI + 2CH_3COOH + 2HNO_2 \longrightarrow 2CH_3COOK + 2NO + 2H_2O + I_2$$

 $I_2 + Starch \longrightarrow Blue colour$ 

(v) Acetate: Acetates when heated with dilute H<sub>2</sub>SO<sub>4</sub> decompose to give acetic acid vapours which possess characteristic smell of vinegar.

(a) All acetates are soluble in water. On addition of neutral FeCl<sub>3</sub> solution to the solution of an acetate, blood red colouration develops due to the formation of ferric acetate.

Note: (i) The ferric chloride solution supplied in the laboratory is always acidic containing HCl. It is made neutral by the addition of dilute solution of NH<sub>4</sub>OH drop by drop with

- constant stirring till the precipitate formed does not dissolve. At this stage filter the solution. The filtrate is called neutral ferric chloride solution.
- (ii) Before testing acetate in the aqueous solution of a salt or a mixture, it must be made sure that the solution does not contain the following ions which also combine with Fe<sup>3+</sup> ions.

(i)  $CO_3^{2-}$ , (ii)  $SO_3^{2-}$ , (iii)  $PO_4^{3-}$ , (iv)  $\Gamma$ 

These ions can be removed by addition of AgNO<sub>3</sub> solution and only after the removal of these ions, the test of acetate should be performed by neutral ferric chloride solution.

(b) Acetates are also decomposed with oxalic acid and give off acetic acid.

$$2CH_3COONa + H_2C_2O_4 \longrightarrow Na_2C_2O_4 + 2CH_3COOH$$

#### **GROUP II**

Take 0.2 g of the substance and add 2 mL of concentrated H<sub>2</sub>SO<sub>4</sub>, warm gently, observe the changes and draw inference as follows:

Note: With concentrated H<sub>2</sub>SO<sub>4</sub>, carbonates, sulphites, sulphides, nitrites and acetates also behave in the same way as with dilute H<sub>2</sub>SO<sub>4</sub>.

~ N				
S. No.	Observation	Inference	Confirmatory tests	
1.	Colourless gas with pungent smell which fumes in air. [Add a pinch of $MnO_2$ in the solution $\longrightarrow$ pale green gas is	Cl <sup>-</sup> (Chloride)	(a) Bring a glass rod dipped in NH <sub>4</sub> OH on the mouth of test tube; white fumes are formed.	
	evolved.]		(b) Bring a glass rod dipped in silver nitrate solution on the mouth- of the test tube; white curdy ppt. is formed on the rod.	
			(c) Chromyl chloride test: To the substance in a dry test tube add three times its weight of powdered K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> and conc. H <sub>2</sub> SO <sub>4</sub> . Heat the contents. Red vapours are evolved. Pass the vapours in a test tube containing NaOH solution. Now add acetic acid and lead acetate solution. A yellow precipitate appears.	
2.	Reddish brown fumes which intensify on addition of MnO <sub>2</sub> . Vapours passed in water, make it yellow.	Br <sup>-</sup> (Bromide)	(a) Take aqueous extract of the substance (or extract with dilute HNO <sub>3</sub> ) and add silver nitrate solution. A light yellow precipitate appears.	
•			(b) To a small amount of the substance add dilute H <sub>2</sub> SO <sub>4</sub> . Warm and cool. Add 1 mL chloroform or carbon tetrachloride and then chlorine water with constant shaking. The chloroform layer becomes orange-brown.	
3.	Violet pungent fumes evolved which may condense as black specks on the cooler parts of the test tube. [The	I <sup>-</sup> (Iodide)	(a) Place a piece of filter paper moistened with starch solution on the mouth of the test tube. The paper turns blue.	
	violet fumes intensify on addition of MnO <sub>2</sub> .]		(b) Take aqueous extract of the substance (or extract with dilute HNO <sub>3</sub> ) and add AgNO <sub>3</sub> solution. Yellow precipitate is formed which is insoluble in NH <sub>4</sub> OH solution.	
*			(c) To the small amount of the substance add dil. H <sub>2</sub> SO <sub>4</sub> and 1 mL of either chloroform or carbon tetrachloride and then chlorine water, shake. Chloroform layer attains violet colouration.	
4.	Light brown vapours having pungent smell. Intensify on adding copper turnings.	NO <sub>3</sub> (Nitrate)	Take an aqueous extract of the substance in a test tube and add freshly prepared FeSO <sub>4</sub> solution. Add conc. H <sub>2</sub> SO <sub>4</sub> by the side of the test tube without disturbing the solution—a brown ring is formed at the junction of two liquids.	
5.	Colourless, odourless gas which burns with blue flame at the mouth of the test tube and turns lime water milky.	$C_2O_4^{2-}$ (Oxalate)	(a) Take the substance, add dil. H <sub>2</sub> SO <sub>4</sub> and heat till there are no more effervescences. Now add MnO <sub>2</sub> (solid)-brisk effervescences.	
			(b) Calcium chloride test, see page 890.	

#### Reactions with explanations

(i) Chloride: Colourless pungent fumes of hydrogen chloride are evolved on heating the solid chloride with conc.  $H_2SO_4$ .

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

(a) Yellowish-green gas of chlorine with suffocating odour is evolved when the solid chloride mixed with manganese dioxide is heated with conc. H<sub>2</sub>SO<sub>4</sub>.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$
  
 $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$ 

(b) The gas evolved by heating chloride with sulphuric acid forms white fumes of ammonium chloride with NH₄OH.

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$
White fumes

(c) The gas evolved by heating chloride with H<sub>2</sub>SO<sub>4</sub> forms a curdy precipitate of silver chloride with silver nitrate solution.

$$AgNO_3 + HCl \longrightarrow AgCl + HNO_3$$

**Note:** The curdy precipitate dissolves in ammonium hydroxide by forming a complex salt.

$$AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O$$

When the solution having the silver complex is acidified with dilute nitric acid, a white precipitate of silver chloride is again formed.

$$Ag(NH_3)_2Cl + 2HNO_3 \longrightarrow AgCl + 2NH_4NO_3$$

(d) Chromyl chloride test: When solid chloride is heated with conc. H<sub>2</sub>SO<sub>4</sub> in presence of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, deep red vapours of chromyl chloride are evolved.

$$\begin{array}{c} \text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl} \\ \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{KHSO}_4 + 2\text{CrO}_3 + \text{H}_2\text{O} \\ \text{CrO}_3 + 2\text{HCl} \longrightarrow \text{CrO}_2\text{Cl}_2 + \text{H}_2\text{O} \\ \text{Chromyl chloride} \end{array}$$

When these vapours are passed through NaOH solution, the solution becomes yellow due to the formation of sodium chromate.

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$
  
Yellow colour

The yellow solution is neutralised with acetic acid and on addition of lead acetate gives a yellow precipitate of lead chromate.

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow PbCrO_4 + 2CH_3COONa$$
  
Yellow ppt.

- Note: (i) This test is not given by the chlorides of mercury, tin, silver, lead and antimony. In such cases this test may be performed by taking the residue obtained after evaporation of sodium carbonate extract.
  - (ii) The chromyl chloride test is always to be performed in a dry test tube; otherwise the chromyl chloride vapours will be hydrolysed in the test tube.

$$CrO_2Cl_2 + 2H_2O \longrightarrow H_2CrO_4 + 2HCl$$

- (iii) The test is said to be positive when all the three observations, viz., orange-yellow (red) vapours of chromyl chloride, yellow solution of sodium chromate, yellow precipitate of lead chromate, are correct.
- (iv) Sometimes, a white precipitate is obtained after the addition of lead acetate solution even in absence of chloride. This may be due to strong heating of the mixture with conc. H<sub>2</sub>SO<sub>4</sub> when H<sub>2</sub>SO<sub>4</sub> vapours are absorbed in NaOH solution or due to incomplete neutralisation of NaOH solution which reacts with lead acetate to form lead hydroxide.
- (v) Bromides and iodides do not give this test.
- (ii) Bromide: Reddish-brown fumes of bromine are formed when the solid bromide is heated with conc.  $H_2SO_4$ .

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$
  
 $2HBr + H_2SO_4 \longrightarrow Br_2 + 2H_2O + SO_2$ 

More reddish-brown fumes of bromine are evolved when MnO<sub>2</sub> is added.

$$2NaBr + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 2HBr$$

$$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + [O]$$

$$2HBr + [O] \longrightarrow H_2O + Br_2$$

$$2\text{NaBr} + \text{MnO}_2 + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{NaHSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O}_4 + \vec{\text{Bi}}_2$$

(a) The aqueous solution of bromide gives pale yellow precipitate of silver bromide which dissolves in excess of NH<sub>4</sub>OH forming a soluble complex. [AgBr is sparingly soluble in NH<sub>4</sub>OH solution.]

$$NaBr + AgNO_3 \longrightarrow AgBr$$
 +  $NaNO_3$  Pale yeliow ppt.

$$AgBr + 2NH_4OH \longrightarrow Ag(NH_3)_2Br + 2H_2O$$

(b) When the fresh salt or mixture is treated with dilute H<sub>2</sub>SO<sub>4</sub>, CHCl<sub>3</sub> or CCl<sub>4</sub> and chlorine water, chlorine replaces bromine and the liberated bromine dissolves in CHCl<sub>3</sub> or CCl<sub>4</sub> layer giving it brown colour.

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$

**Note:** Excess of chlorine water should not be used. Under this condition the layer attains either pale yellow colour due to formation of bromine monochloride or it becomes colourless due to formation of hypobromous acid.

$$\begin{array}{ccc} Br_2 + Cl_2 & \longrightarrow & 2Br \cdot Cl \\ & \text{Bromine monochloride} \\ Br_2 + 2H_2O + Cl_2 & \longrightarrow & 2HBrO \\ & \text{Hypobromous acid} \end{array} + 2HCl_2$$

(iii) **Iodide:** Violet vapours of iodine are evolved on heating iodide with concentrated  $H_2SO_4$ .

$$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$
  
 $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O_3$ 

More violet vapours are evolved when MnO2 is added.

$$2KI + 2H2SO4 \longrightarrow 2KHSO4 + 2HI$$

$$MnO2 + H2SO4 \longrightarrow MnSO4 + H2O + [O]$$

$$2HI + [O] \longrightarrow H2O + I2$$

$$2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2$$

(a) Violet vapours with starch produce blue colour.

$$I_2$$
 + Starch  $\longrightarrow$  Blue colour

(b) Aqueous solution of the iodine gives yellow precipitate of AgI with silver nitrate solution which does not dissolve in NH<sub>4</sub>OH.

$$NaI + AgNO_3 \longrightarrow AgI + NaNO_3$$
  
Yellow ppt.

(c) When the given substance is treated with dilute H<sub>2</sub>SO<sub>4</sub>, CHCl<sub>3</sub> or CCl<sub>4</sub> and chlorine water, chlorine replaces iodine which dissolves in CHCl<sub>3</sub> or CCl<sub>4</sub> layer giving it violet colour.

$$2KI + Cl_2 \longrightarrow 2KCI + I_2$$
  
 $I_2 + CHCl_3 \longrightarrow Violet layer$ 

**Note:** Excess of chlorine water should be avoided as the layer becomes colourless with the conversion of iodine into iodic acid.

$$[Cl2 + H2O \longrightarrow 2HCl + O] \times 5$$

$$I2 + H2O + 5[O] \longrightarrow 2HIO3$$

$$I2 + 5Cl2 + 6H2O \longrightarrow 2HIO3 + 10HCl$$

(iv) Nitrate: Light brown fumes of nitrogen dioxide are evolved on heating the nitrate with concentrated H<sub>2</sub>SO<sub>4</sub>.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$
  
 $4HNO_3 \longrightarrow 2H_2O + 4NO_2 + O_2$ 

These fumes intensify when copper turnings are added.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Ring Test: When the aqueous solution of the substance is treated with freshly prepared solution of ferrous sulphate and conc. H<sub>2</sub>SO<sub>4</sub>, a brown ring is formed on account of the formation of a complex at the junction of two liquids.

$$\begin{array}{c} NaNO_3 \,+\, H_2SO_4 \longrightarrow \, NaHSO_4 \,+\, HNO_3 \\ 6FeSO_4 \,+\, 2HNO_3 \,+\, 3H_2SO_4 \longrightarrow \, 3Fe_2(SO_4)_3 + 4H_2O + 2NO \\ [Fe(H_2O)_6]SO_4 \cdot H_2O \,+\, NO \,\longrightarrow \, [Fe(H_2O)_5NO]SO_4 + 2H_2O \\ \text{Ferrous sulphate} \end{array}$$

Note: (a) Ring test is not reliable in presence of nitrite, bromide and iodide.

(b) The nitrates can be tested by boiling nitrate with Zn or Al in presence of concentrated NaOH solution when ammonia is evolved which can be detected by the characteristic odour.

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + 2H$$
  
 $Al + NaOH + H_2O \longrightarrow NaAlO_2 + 3H$   
 $NaNO_3 + 8H \longrightarrow NaOH + 2H_2O + NH_3$ 

(v) Oxalate: When oxalate is heated with conc. H<sub>2</sub>SO<sub>4</sub>, a mixture of CO and CO<sub>2</sub> is given off. The CO burns with blue flame.

$$Na_2C_2O_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2C_2O_4$$
  
 $H_2C_2O_4 + [H_2SO_4] \longrightarrow CO + CO_2 + H_2O + [H_2SO_4]$ 

#### **GROUP III**

Some anions are identified by their characteristic chemical reactions. These radicals are sulphate, borate, phosphate and fluoride.

(i) Sulphate: Dissolve a little amount of the substance (salt or mixture) and add barium chloride solution. A white precipitate insoluble in conc. HNO<sub>3</sub> is formed.

#### Reactions with explanations

White precipitate of barium sulphate is obtained when soluble sulphate is treated with barium chloride solution.

$$Na_2SO_4 + BaCl_2 \longrightarrow 2NaCl + BaSO_4$$
  
White ppt

The white precipitate is insoluble in conc. HNO<sub>3</sub>. Certain chlorides, e.g., NaCl and BaCl<sub>2</sub> when present in large quantities, may form a white precipitate which dissolves on dilution with water.

Silver and lead, if present, may be precipitated as silver chloride and lead chloride by the addition of barium chloride. To avoid it, barium nitrate may be used in place of barium chloride.

(ii) Borate: To a small quantity of the substance (salt or mixture), add a few mL of ethyl alcohol and conc. H<sub>2</sub>SO<sub>4</sub>. Stir the contents with a glass rod. Heat the test tube and bring the mouth of the test tube near the flame. The formation of green edged flame indicates the presence of borate.

#### Reactions with explanations

When borate is heated with ethyl alcohol and H<sub>2</sub>SO<sub>4</sub>, ethyl borate vapours come out which burn with green edged flame.

$$2Na_3BO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2H_3BO_3$$

$$H_3BO_3 + 3C_2H_5OH \longrightarrow (C_2H_5)_3BO_3 + 3H_2O$$
Ethyl borate

In place of ethyl alcohol, methyl alcohol can also be used. This test should be performed in a test tube and not in a porcelain basin because copper or barium salts, if present, will come in contact with the flame which also give green flame.

(iii) Phosphate: Take about 0.2 g of the substance in a test tube and add 2 mL conc. HNO<sub>3</sub>. Heat and add 2 mL ammonium molybdate solution. Again heat. A canary yellow precipitate indicates the presence of phosphate.

#### Reactions with explanations

The canary yellow precipitate is due to the formation of ammonium phosphomolybdate.

$$Ca_{3}(PO_{4})_{2} + 6HNO_{3} \longrightarrow 3Ca(NO_{3})_{2} + 2H_{3}PO_{4}$$

$$H_{3}PO_{4} + 12(NH_{4})_{2}MoO_{4} + 21HNO_{3} \longrightarrow (NH_{4})_{3} \cdot PO_{4} \cdot 12MoO_{3}$$

$$(Canary yellow ppt.)$$

$$+ 21NH_{4}NO_{3} + 12H_{2}O$$

Arsenic under similar conditions also yields a yellow precipitate of (NH<sub>4</sub>)<sub>3</sub>·AsO<sub>4</sub>·12MoO<sub>3</sub> (ammonium arsenomolybdate). So, in presence of As, phosphate is tested in the filtrate of second group.

(a) The precipitate of ammonium phosphomolybdate dissolves in excess of phosphate. Thus, the reagent (ammonium molybdate) should always be added in excess.

- (b) HCl interferes in this test. Hence, if the test of phosphate is to be performed with the solution containing HCl, the solution should be boiled to remove HCl.
- (c) Reducing agents such as sulphites, sulphides, etc., interfere as they reduce Mo(VI) to molybdenum blue  $(Mo_3O_8.xH_2O)$ . The solution, therefore, turns blue. In the presence of reducing agents, the solutions should be boiled with  $HNO_3$  as to oxidise them before the addition of ammonium molybdate.
- (iv) Fluoride: Take a small amount of the substance in a dry test tube and add an equal amount of sand. Mix the contents and add conc. H<sub>2</sub>SO<sub>4</sub>. Heat the contents and place a glass rod moistened with water over the mouth of the test tube. A waxy white deposit on the rod is formed.

#### Reactions with explanations

The fluoride with conc. H<sub>2</sub>SO<sub>4</sub> forms H<sub>2</sub>F<sub>2</sub> (hydrofluoric acid) which attacks silica forming silicon tetrafluoride, SiF<sub>4</sub>. The vapours of SiF<sub>4</sub> are hydrolysed by H<sub>2</sub>O into gelatinous silicic acid which is deposited on the rod.

$$\begin{array}{c} 2\text{NaF} + \text{H}_2\text{SO}_4 & \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{F}_2 \\ \text{SiO}_2 + 2\text{H}_2\text{F}_2 & \longrightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \\ 3\text{SiF}_4 + 4\text{H}_2\text{O} & \longrightarrow \text{H}_4\text{SiO}_4 + 2\text{H}_2\text{SiF}_6 \\ & \text{Silicic acid} \\ \text{(White)} \end{array}$$

- (a) The test should be performed in perfectly dry test tube, otherwise waxy white deposit will not be formed on the rod.
- (b) HgCl<sub>2</sub> and NH<sub>4</sub>Cl also produce a deposit under these conditions, but this deposit is crystalline in nature.

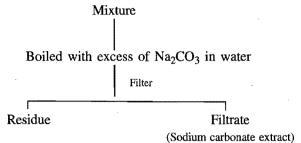
### 18.3 IDENTIFICATION OF ACIDIC RADICALS WITH SODIUM CARBONATE EXTRACT

A large number of acidic radicals can be confirmed by using sodium carbonate extract of the mixture. One part of the given substance is mixed with about 3 parts of sodium carbonate and nearly 10 to 15 mL of distilled water. The contents are then heated for 10–15 minutes and filtered. The filtrate is known as sodium carbonate extract or soda extract.

During the heating of mixture with sodium carbonate, double decomposition takes place, *i.e.*, exchange of partners takes place.

For example,

Thus, carbonates of the cations of the mixture are formed which are mostly insoluble in water and are obtained in the residue. On the other hand, sodium salts of the anions (acidic radicals) of the mixture are formed which being soluble in water are obtained in the filtrate.



Sodium carbonate extract (filtrate) contains:

- (i) Sodium salts of acidic radicals present in the mixture.
- (ii) Unused sodium carbonate and
- (iii) Some soluble compounds like (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>,K<sub>2</sub>CO<sub>3</sub>, NaAlO<sub>2</sub>, etc.

The sodium carbonate extract is basic in nature and before it is used for the detection and identification of a particular acidic radical, it is first neutralised by the addition of small quantity of an appropriate acid. The acid is added to the extract till the effervescences cease to evolve.

Neutralisation is done according to the following scheme:

Radicals to be tested	Acid used for neutralization	Reagents for testing
Chloride	Dilute HNO <sub>3</sub>	AgNO <sub>3</sub>
Bromide	Dilute HNO <sub>3</sub>	AgNO <sub>3</sub>
Iodide.	Dilute HNO <sub>3</sub>	AgNO <sub>3</sub>
Sulphate	Dilute HCl	· BaCl <sub>2</sub>
Oxalate	Acetic acid	CaCl <sub>2</sub>
Sulphite	Dilute HCl	BaCl <sub>2</sub>

#### Advantages of preparing sodium carbonate extract:

- (i) Many salts are insoluble in water and dilute acids. The preparation of sodium carbonate extract affords a convenient method for bringing the anions of the mixture in solution.
- (ii) It removes the basic radicals (usually coloured) which could have interfered in the usual tests of some of the acidic radicals.
- (iii) The residue can be used for the tests of basic radicals of I to VI groups as it can be easily dissolved in dil. HCl or conc. HCl. Such a solution does not involve the problem of removing interfering radicals like oxalate, fluoride, borate and phosphate.

### Tests of various acidic radicals with sodium carbonate extract:

(i) Sulphide: (a) Take sodium carbonate extract and add few drops of NaOH and then freshly prepared sodium nitroprusside solution. Appearance of violet colour indicates the presence of sulphide.

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$$
  
Sodium nitroprusside (Violet colour)

(b) To soda extract, add lead acetate solution. A black precipitate indicates the presence of sulphide.

$$Na_2S + Pb(CH_3COO)_2 \longrightarrow PbS + 2CH_3COONa$$

$$\underset{(Black)}{\longleftarrow} + 2CH_3COONa$$

(c) To soda extract add cadmium carbonate. A yellow precipitate indicates the presence of sulphide.

$$Na_2S + CdCO_3 \longrightarrow CdS + Na_2CO_3$$

$$Cadmium sulphide (Yellow)$$

(ii) Sulphite: Acidify the soda extract with dilute HCl and add barium chloride solution followed by bromine water and heat the contents. Appearance of white precipitate indicates the presence of sulphite.

$$\begin{array}{c} \text{Na}_2\text{SO}_3 + \text{BaCl}_2 \longrightarrow \text{BaSO}_3 + 2\text{NaCl} \\ \hline \text{Br}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HBr} + \text{O} \\ \hline \text{BaSO}_3 + \text{O} \longrightarrow \text{BaSO}_4 \\ \text{White ppt.} \end{array}$$

(iii) Sulphate: Acidify the soda extract with dilute HCl or dilute HNO<sub>3</sub> and add barium chloride solution. A white precipitate insoluble in concentrated HCl and concentrated HNO<sub>3</sub> indicates the presence of sulphate.

$$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2NaCl$$
White ppt.

(iv) Nitrite: Acidify soda extract with acetic acid and add concentrated solution of cobalt chloride. Then add potassium chloride. Warm the contents and wait for sometime. Appearance of yellow precipitate indicates the presence of nitrite.

$$\begin{array}{c} CoCl_2 + 2NaNO_2 \longrightarrow Co(NO_2)_2 + 2NaCl \\ NaNO_2 + CH_3COOH \longrightarrow CH_3COONa + HNO_2 \\ 2HNO_2 \longrightarrow H_2O + 2NO + [O] \\ 2Co(NO_2)_2 + 2NaNO_2 + H_2O + [O] \rightarrow 2Co(NO_2)_3 + 2NaOH \\ Co(NO_2)_3 + 3NaNO_2 \longrightarrow Na_3[Co(NO_2)_6] \\ Colourless and soluble \\ Na_3[Co(NO_2)_6] + 3KCl \longrightarrow K_3[Co(NO_2)_6] + 3NaCl \\ Potassium cobaltinitrite \\ (Yellow and insoluble) \end{array}$$

(v) Chloride: Acidify sodium carbonate extract with dilute nitric acid and add silver nitrate solution. A white precipitate of silver chloride is formed which dissolves in ammonium hydroxide.

$$NaCl + AgNO_{3} \longrightarrow \underset{White \ ppt.}{AgCl} + NaNO_{3}$$

(vi) **Bromide:** (a) Acidify the sodium carbonate extract with dilute HNO<sub>3</sub> and add silver nitrate solution. A light yellow precipitate of silver bromide is formed which is sparingly soluble in ammonium hydroxide.

NaBr + AgNO<sub>3</sub> 
$$\longrightarrow$$
 AgBr + NaNO<sub>3</sub>  
Silver bromide  
(Pale yellow ppt.)

(b) Take the second part of the sodium carbonate extract and add  $CHCl_3$  or  $CCl_4$  and then chlorine water. Shake the contents. The chloroform layer turns brown.

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$$
  
 $Br_2 + Chloroform \longrightarrow Brown layer$ 

Note: In place of chlorine water, conc. HNO3 can be used.

(vii) Iodide: (a) Acidify sodium carbonate extract with dilute HNO<sub>3</sub> and add silver nitrate solution. A yellow precipitate of silver iodide appears which does not dissolve in ammonium hydroxide.

$$AgNO_3 + NaI \longrightarrow AgI + NaNO_3$$
  
Yellow ppt.

(b) Take the second part of the soda extract and add chloroform or carbon tetrachloride and then chlorine water. Shake vigorously. The chloroform layer turns violet.

Note: In place of chlorine water, conc. HNO3 can be used.

(viii) Oxalate: Acidify the sodium carbonate extract with acetic acid and add CaCl<sub>2</sub> solution. A white precipitate is obtained. Filter and dissolve the precipitate in dilute H<sub>2</sub>SO<sub>4</sub> and add fewdrops of potassium permanganate solution. The colour of KMnO<sub>4</sub> is discharged. This indicates the presence of oxalate.

$$\begin{array}{c} Na_2C_2O_4 + CaCl_2 \longrightarrow CaC_2O_4 + 2NaCl \\ & \text{White ppt.} \\ CaC_2O_4 + H_2SO_4 \longrightarrow H_2C_2O_4 + CaSO_4 \\ & \text{Calcium oxalate} \\ \hline 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \\ & COOH \\ & | & + [O] \longrightarrow 2CO_2 + H_2O \\ & COOH \\ \end{array}$$

Note: In presence of fluoride, a white precipitate of CaF<sub>2</sub> is also formed by the addition of CaCl<sub>2</sub> solution. But CaF<sub>2</sub> does not dissolve in dil. H<sub>2</sub>SO<sub>4</sub> and does not discharge the colour of KMnO<sub>4</sub>.

#### 18.4. IDENTIFICATION OF BASIC RADICALS

Wet test analysis for basic radicals includes the following steps:

- (a) Preparation of the original solution of the salt or mixture.
  - (b) Separation of basic radicals into different groups.
- (c) Analysis of the precipitates obtained in different groups and confirmation of the basic radicals by specific tests.

#### (a) Preparation of the original solution

The following solvents should be tried strictly in the order given below:

- (i) Cold water,
- (ii) Hot water,
- (iii) Dilute HCl,
- (iv) Concentrated HCl.

- (i) Take about 0.1 g of salt or mixture in a test tube and shake it with 3.4 mL cold distilled water.
- (ii) If the substance is insoluble, heat to boil the contents and shake.
- (iii) If the substance does not dissolve, take fresh quantity about 0.1 g of salt or mixture in a test tube and add about 3 mL dilute HCl and shake. If the substance is insoluble, boil the contents.
- (iv) If the substance is still insoluble, treat fresh amount of 0.1 g of salt or mixture with 2 mL of conc. HCl. Heat to boiling, dilute with 5 mL distilled water and again heat. This treatment will dissolve most of the substances.

After selecting a suitable solvent for the given salt or mixture, take about 10 mL of the solvent in a boiling test tube, heat to boiling, add the solid substance little by little. Continue heating and adding the mixture till a concentrated solution is obtained. Dilute the solution with equal amount of water.

If the solution is to be prepared in concentrated HCl, take about 1.0 g of solid substance in a basin, add 5 mL of concentrated HCl. Evaporate to dryness. Add 1 mL of concentrated HCl to solid residue and 20 mL of distilled water. The solution thus obtained is called the original solution.

**Note:** (i) When the salt or mixture is soluble in cold dilute HCl, it shows that basic radicals Pb<sup>2+</sup>, Hg<sub>2</sub><sup>2+</sup> and Ag<sup>+</sup> are absent.

- (ii) Lead chloride, PbCl<sub>2</sub>, is soluble in hot solution but insoluble in cold solution. Thus, when the hot solution is cooled, if a white substance appears, it shows the presence of Pb<sup>2+</sup>.
- (iii) Sometimes, a white precipitate or milkiness is formed when the solution prepared in concentrated HCl is diluted, even when no member of first group is present. This may be due to formation of the oxychlorides of antimony, bismuth and tin.
   BiCl<sub>3</sub> + H<sub>2</sub>O → BiOCl + 2HCl White ppt.

The precipitate disappears if little concentrated HCl is added. In such a case, H<sub>2</sub>S can be passed through milky solution.

$$2BiOCl + 3H_2S \longrightarrow Bi_2S_3 + 2HCl + 2H_2O$$

- (iv) A white crystalline precipitate of NaCl and BaCl<sub>2</sub> may be formed from the concentrated solution by the addition of concentrated HCl due to common ion effect. Such precipitates dissolve on dilution.
- (v) The original solution should not be prepared in concentrated nitric acid and concentrated H<sub>2</sub>SO<sub>4</sub>. These act as oxidising agents and convert H<sub>2</sub>S into S-in second group. Nitric acid converts sulphides of Ba, Sr, and Pb into insoluble sulphates. Similarly sulphuric acid converts the salts of Ba, Sr and Pb into insoluble sulphates.

### (b) Separation of basic radicals into different groups

For systematic analysis, the basic radicals have been classified into groups. Each group has a reagent, which shows the presence of the basic radical belonging to that particular group. It is necessary that the radical is completely removed in the respective group by using excess of group reagent, otherwise its presence creates difficulty in higher group.

Group	Group reagent	Basic radical	Composition and colour of the precipitate	
1.	Dilute HCl	$Ag^{+}$	AgCl: white	Chlorides
		Pb <sup>2+</sup>	PbCl <sub>2</sub> : white	insoluble in
		Hg <sub>2</sub> <sup>2+</sup>	Hg <sub>2</sub> Cl <sub>2</sub> : white	cold dilute HCl
2.	H <sub>2</sub> S in	Hg <sup>2+</sup>	HgS: black	,
•	presence of	Pb <sup>2+</sup>	PbS: black	*
	dilute HCl	Bi <sup>3+</sup>	Bi <sub>2</sub> S <sub>3</sub> : black	
		Cu <sup>2+</sup>	CuS: black	Sulphides
		$Cd^{2+}$	CdS: yellow	insoluble in
•		As <sup>3+</sup>	As <sub>2</sub> S <sub>3</sub> : yellow	dilute HCl
·····		Sb <sup>3+.</sup>	Sb <sub>2</sub> S <sub>3</sub> :-orange	
	, ,	Sn <sup>2+</sup>	SnS: brown	
		Sn <sup>4+</sup>	SnS <sub>2</sub> : yellow	
3.	NH <sub>4</sub> OH in	Fe <sup>3+</sup>	Fe(OH) <sub>3</sub> :	<u>.</u> ]
	presence of		reddish brown	Hydroxides
	NH <sub>4</sub> Cl	Cr <sup>3+</sup>	Cr(OH) <sub>3</sub> : green	are insoluble — in NH <sub>4</sub> OH
٠.		Al <sup>3+</sup>	Al(OH) <sub>3</sub> : white	
4.	H <sub>2</sub> S in presence of	Zn <sup>2+</sup>	ZnS: greenish white	
	NH <sub>4</sub> OH	Mn <sup>2+</sup>	MnS: buff	Sulphides are insoluble in
*		Co <sup>2+</sup>	CoS: black	NH <sub>4</sub> OH
		Ni <sup>2+</sup>	NiS: black	
5.	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> in	Ba <sup>2+</sup>	BaCO <sub>3</sub> : white	]
	presence of	Sr <sup>2+</sup>	SrCO <sub>3</sub> : white	Carbonates are insoluble
	NH <sub>4</sub> OH	Ca <sup>2+</sup>	CaCO <sub>3</sub> : white	are moorable
6.	Na <sub>2</sub> HPO <sub>4</sub>	Mg <sup>2+</sup>	Mg(NH <sub>4</sub> )PO <sub>4</sub> : white	
7.	NaOH	NH <sub>4</sub>	Ammonia gas is evolved.	

### (c) Detection of basic radicals GROUP I

**Radicals:**  $Pb^{2+}$ ,  $Ag^+$ ,  $Hg_2^{2+}$  (ous)

Group reagent: Dil. HCl

**Procedure:** Take cold dilute original solution and add few drops of dilute HCl. If white precipitate appears, add more of dilute HCl as to complete precipitation of basic radicals of first group. Filter, keep the filtrate for subsequent groups.

Wash the precipitate with cold water. Transfer precipitate in a test tube and add about 10 mL of water, boil. If the precipitate dissolves, Pb<sup>2+</sup> is present and if it does not dissolve, it may have Ag<sup>+</sup> or Hg<sub>2</sub><sup>2+</sup>. If the precipitate does not dissolve, filter it.

When the preci- pitate dissolves in hot water	Solid residue (insoluble in hot water), add hot NH <sub>4</sub> OH		
Divide the filtrate in four parts.  (i) First part—cool under tap water—white crystalline ppt. of PbCl <sub>2</sub> .  (ii) Second part +K <sub>2</sub> CrO <sub>4</sub> soln. —yellow ppt. of PbCrO <sub>4</sub> (iii) Third part + KI solution —yellow ppt. of PbI <sub>2</sub>	most of the acids, dilute with water and divide into two parts: Part I: Add stannous chloride solution. A white precipitate appears which turns grey. Part II: Add copper turnings. A grey deposit is formed on	dissolves. Divide the solution into two parts: First part + dil. HNO <sub>3</sub>	
acetate.  Pb <sup>2+</sup> confirmed	Hg <sub>2</sub> <sup>2+</sup> (ous) confirmed		

#### **GROUP II**

**Radicals :**  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Bi^{3+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$  Group IIA  $As^{3+}$ ,  $Sb^{3+}$ ,  $Sn^{2+}$ ,  $Sn^{4+}$  Group IIB

Group reagent: H<sub>2</sub>S gas in presence of dil. HCl

**Procedure:** Warm a part of the filtrate of first group or original solution containing dilute HCl (if first group is absent) and pass H<sub>2</sub>S gas. If a precipitate (black or brown or yellow or orange) appears, pass H<sub>2</sub>S through whole of the solution. Filter, dilute the filtrate, warm and again pass H<sub>2</sub>S. Filter. Repeat this process till the precipitation is complete. Keep the filtrate for subsequent groups.

Wash the precipitate with hot water. Take small part of the precipitate in a test tube and add about 5 mL of yellow ammonium sulphide solution, warm upto 60°C with shaking.

If the precipitate does not dissolve, Group IIA radical may be present.

If the precipitate dissolves, Group IIB radical may be present.

Insoluble in yellow ammonium sulphide	Soluble in yellow ammonium sulphide
IIA Group HgS Black PbS Black Bi <sub>2</sub> S <sub>3</sub> Black CuS Black CdS Yellow	IIB Group As <sub>2</sub> S <sub>3</sub> Yellow Sb <sub>2</sub> S <sub>3</sub> Orange SnS Brown SnS <sub>2</sub> Yellow

Note: (i) Before passing H<sub>2</sub>S, the acidic concentration of the solution should be properly adjusted. If the solution is too acidic, lead and cadmium will not be precipitated. On the other hand if too little HCl is used, zinc will also be precipitated. The proper hydrogen ion concentration is 0.25 N to 0.5 N with respect to HCl.

- (ii) The original solution must be free from any oxidising agent otherwise H<sub>2</sub>S gets oxidised with precipitation of free sulphur. This is done by heating the mixture with concentrated HCl for sufficient time during preparation of original solution. This treatment will also remove sulphite, nitrite from the mixture which can oxidise H<sub>2</sub>S.
- (iii) Hydrogen sulphide should be passed slowly in hot solution to get granular and easily filterable precipitate.

#### **GROUP IIA**

**Procedure:** Take the precipitate (if insoluble in yellow ammonium sulphide) in a test tube add 5 mL of dilute HNO<sub>3</sub>. Boil for few minutes. If insoluble, filter it.

Insoluble (black) HgS. Dissolve it in aqua-regia and divide into two parts:  Part I: Add SnCl <sub>2</sub> solution — a white ppt. which changes into greyish coloured ppt.  Part II: Add Cuturnings — a greyish deposit on copper	Soluble—It may have Pb <sup>2+</sup> , Cu <sup>2+</sup> , Bi <sup>3+</sup> or Cd <sup>2+</sup> Divide the solution into two parts:  First part: Add dilute H <sub>2</sub> SO <sub>4</sub> and alcohol.  The appearance of white precipitate confirms the presence of lead. In case no precipitate, use second part of filtrate.  Second part of filtrate + excess of NH <sub>4</sub> OH soln.  White precipitate (then filter) or blue-coloured solution or colourless solution.		
deposit on copper turnings.	White	Blue coloured	Colourless
Hg <sup>2+</sup> (ic) confirmed	precipitate	solution	solution
	Dissolve the ppt. in dilute HCl and divide into three parts: Part I: Add sodium stannite solution — black ppt. Part II: Dilute with water — white ppt. Part III: Add a little 10% thiourea soln. — Yellow colouration.	Acidify the solution with acetic acid and add K4[Fe(CN)6] soln. ————————————————————————————————————	through soln.  Appe-

Note: (i) Sodium stannite is prepared by taking 1 mL of stannous chloride and adding to it drop by drop NaOH till the precipitate formed dissolves.

Bi<sup>3+</sup>present

$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$$
 $ppt.$ 
 $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$ 
 $Sodium stannite$ 
 $(soluble)$ 

(ii) Yellow ammonium sulphide is used only for one radical, i.e., Sn<sup>2+</sup> which is not soluble in ordinary ammonium sulphide. Yellow ammonium sulphide consists excess of sulphur and is formulated as (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>, commonly as (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>. This converts SnS first into SnS<sub>2</sub> which then dissolves forming thio complex. In case Sn<sup>2+</sup> is absent, ordinary ammonium sulphide can be used in place of yellow ammonium sulphide.

#### **GROUP IIB**

**Procedure:** Take the remaining precipitate (if the precipitate is soluble in yellow ammonium sulphide) and add 1 mL of concentrated HCl and boil. If the precipitate is insoluble, filter and test for arsenic and in case dissolves, test for antimony and tin.

Insoluble in conc. HCl	Soluble in conc. HCl		
Dissolve the yellow ppt. in conc. HNO <sub>3</sub> .	Dilute the solution with water. Divide the solution in two parts.		
Add ammonium molybdate and again heat $\longrightarrow$ yellow ppt. As <sup>3+</sup> confirmed	First part: Add NH <sub>4</sub> OH and pass H <sub>2</sub> S $\longrightarrow$ orange ppt. Sb <sup>3+</sup> confirmed	Second part: Add iron fillings and heat for 10 minutes. Filter into a solution of	
		mercuric chloride  → A white ppt. turning grey, Sn <sup>2+</sup> confirmed	

#### **GROUP III**

**Radicals:**  $Fe^{3+}$ ,  $Al^{3+}$ ,  $Cr^{3+}$ 

 $\textbf{Group reagent:} \quad NH_4OH \, + \, NH_4Cl$ 

**Procedure:** Boil off  $H_2S$  from the filtrate of II group or take original solution if first and second group radicals are absent. Add few drops of concentrated  $HNO_3$  and boil the solution. Add 10 g solid ammonium chloride and ammonium hydroxide slowly till the solution smells of ammonia. If the precipitate appears, filter. The filtrate should be kept for subsequent groups.

Reddish brown ppt. Fe(OH) <sub>3</sub>	Green precipitate Cr(OH) <sub>3</sub>	White precipitate Al(OH) <sub>3</sub>
Dissolve the ppt. in dilute HCl and divide into two parts:  Part I + K <sub>4</sub> Fe(CN) <sub>6</sub> soln.    Prussian blue solution or ppt. Part II + KCNS soln.    Red colouration.    Fe <sup>3+</sup> confirmed	ppt. + NaOH + Br <sub>2</sub> water → Yellow soln. Acidify the yellow solution with acetic acid and add lead acetate solution → Yellow ppt. Cr³+ confirmed	Dissolve the ppt. in dil. HCl. Add NaOH solution — White ppt. appears which then dissolves in excess of NaOH. Treat this solution with solid ammonium chloride — Gelatinous white
		precipitate.  Al <sup>3+</sup> confirmed

Note: (i) H<sub>2</sub>S must be completely removed, otherwise the sulphides of the IV group will be precipitated here.

(ii) A very small amount of HNO<sub>3</sub> should be used, otherwise manganese from divalent state (Mn<sup>2+</sup>) is oxidised to trivalent state (Mn<sup>3+</sup>) which may get precipitated as Mn(OH)<sub>3</sub>.

(iii) Precipitation should be done in hot condition and large excess of NH<sub>4</sub>OH should not be used. Ammonium chloride should always be added before the addition of ammonium hydroxide.

#### **GROUP IV**

**Radicals:** Ni<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>

Group reagent:  $H_2S$  gas in presence of  $NH_4Cl$  and  $NH_4OH$ 

**Procedure:** Take the filtrate of third group, concentrate it by heating. Add ammonium hydroxide and again heat the solution. Pass H<sub>2</sub>S gas. If the precipitate appears, pass H<sub>2</sub>S gas for sufficient time and then filter. Keep the filtrate for subsequent groups.

Black precipitate NiS or CoS	Buff coloured precipitate, MnS	White precipitate ZnS
Wash the ppt. with hot	Dissolve in HCl (dil.).	Dissolve the ppt. in
water and dissolve it	Add NaOH to the	dilute HCl and add
in aqua-regia and	clear solution and	NaOH drop by drop.
evaporate to dryness.	then Br <sub>2</sub> water. Boil	The precipitate formed
Extract the residue	and filter. The ppt. is	dissolves in NaOH.
with water or dilute	treated with conc.	Pass H <sub>2</sub> S gas through
HCl. Divide it into	HNO3 and PbO2 or	this solution $\longrightarrow$
two parts.	Pb <sub>3</sub> O <sub>4</sub> (red lead).	Appearance of white
Part I + dimethyl	The contents are	ppt.
glyoxime + NH <sub>4</sub> OH	heated. Keep the test	Zn <sup>2+</sup> confirmed
→ Orange ppt.	tube for some time	
Ni <sup>2+</sup> confirmed	→ Purple coloured	
Part II + NH <sub>4</sub> SCN	solution.	
$(solid) + Acetone \longrightarrow$	Mn <sup>2+</sup> confirmed	•
Blue layer.	*	
Co <sup>2+</sup> confirmed		

#### GROUP V

Radicals: Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>

Group reagent: (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in presence of NH<sub>4</sub>OH

**Procedure:** Take the filtrate of fourth group. Boil off H<sub>2</sub>S gas and concentrate to about 1/2 of its volume. Add a little solid NH<sub>4</sub>Cl and NH<sub>4</sub>OH followed by (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution. Appearance of white precipitate shows the presence of V group. Filter and keep the filtrate for VI group. The white precipitate may be either of BaCO<sub>3</sub> or SrCO<sub>3</sub> or CaCO<sub>3</sub>. Dissolve the precipitate in minimum quantity of acetic acid. Divide the solution into three parts.

1st part + K <sub>2</sub> CrO <sub>4</sub>	If Ba <sup>2+</sup> is absent, use	If Ba <sup>2+</sup> and Sr <sup>2+</sup> both
soln. → Yellow	2nd part. Add	are absent, use the 3rd
precipitate.	$(NH_4)_2SO_4$ solution	part.
Ba <sup>2+</sup> present	→ White precipitate.	Add $(NH_4)_2C_2O_4$
	Sr <sup>2+</sup> present	
-		Ca <sup>2+</sup> present

#### **GROUP VI**

Radical: Mg<sup>2+</sup>

Group reagent: Na<sub>2</sub>HPO<sub>4</sub> in presence of NH<sub>4</sub>OH

**Procedure:** Take the filtrate of V group and add a little NH<sub>4</sub>OH and then Na<sub>2</sub>HPO<sub>4</sub> solution. Scratch the walls of the test tube by a glass rod and allow to stand. Appearance of white precipitate confirms the presence of Mg<sup>2+</sup>.

**Test for NH** $_4^+$ : Take the mixture in a test tube and add 2-3 mL NaOH solution and heat. If the smell of NH $_3$  is observed, it confirms the presence of NH $_4^+$  ion. The confirmation can further be done by the following tests:

- (i) Bring a rod dipped in HCl near the mouth of test tube; white dense fumes are formed.
- (ii) Take aqueous solution of mixture and add Nessler's reagent. Appearance of brown colour or precipitate confirms the presence of NH<sub>4</sub><sup>+</sup> ion.

### 18.5 CHEMICAL REACTIONS INVOLVED IN THE TESTS OF BASIC RADICALS

#### **Group I**

When dil. HCl is added to original solution, insoluble chlorides of lead, silver and mercurous mercury are precipitated.

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$$
  
 $AgNO_3 + HCl \longrightarrow AgCl + HNO_3$   
 $Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 + 2HNO_3$ 

#### Pb<sup>2+</sup> (lead)

- (i) PbCl<sub>2</sub> is soluble in hot water and on cooling white crystals are again formed.
- (ii) The solution of PbCl<sub>2</sub> gives a yellow precipitate with potassium chromate solution which is insoluble in acetic acid but soluble in sodium hydroxide.

$$\begin{array}{c} PbCl_2 \, + \, K_2CrO_4 \longrightarrow & PbCrO_4 \, + \, 2KCl \\ & \quad \ Yellow \ ppt. \end{array}$$

$$PbCrO_4 + 4NaOH \longrightarrow Na_2PbO_2 + Na_2CrO_4 + 2H_2O$$

(iii) The solution of PbCl<sub>2</sub> forms a yellow precipitate with potassium iodide solution.

$$PbCl_2 + 2KI \longrightarrow PbI_2 + 2KCl$$
  
Yellow ppt.

(iv) White precipitate of lead sulphate is formed with dilute H<sub>2</sub>SO<sub>4</sub>. The precipitate is soluble in ammonium acetate.

$$PbCl_2 + H_2SO_4 \longrightarrow PbSO_4 + 2HCl$$
  
 $PbSO_4 + 2CH_3COONH_4 \longrightarrow Pb(CH_3COO)_2 + (NH_4)_2SO_4$ 

#### Ag<sup>+</sup> (silver)

(i) AgCl dissolves in ammonium hydroxide.

$$\begin{array}{c} AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O \\ \text{Diammine silver (I)} \\ \text{chloride} \end{array}$$

(ii) On adding dilute HNO<sub>3</sub> to the above solution, white precipitate is again obtained.

$$Ag(NH_3)_2Cl + 2HNO_3 \longrightarrow AgCl + 2NH_4NO_3$$
  
White ppt.

(iii) On adding KI to the complex solution, yellow precipitate is obtained.

$$Ag(NH_3)_2Cl + KI \longrightarrow AgI + KCl + 2NH_3$$
  
Yellow ppt.

#### Hg<sub>2</sub><sup>2+</sup> (mercurous)

(i) Hg<sub>2</sub>Cl<sub>2</sub> turns black with NH<sub>4</sub>OH.

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underbrace{Hg + Hg(NH_2)Cl}_{Black} + NH_4Cl + 2H_2O$$

(ii) The black residue dissolves in aqua-regia forming mercuric chloride.

$$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl$$
 $2Hg(NH_2)Cl + 6Cl \longrightarrow 2HgCl_2 + 4HCl + N_2$ 
 $Hg + 2Cl \longrightarrow HgCl_2$ 

(iii) The solution of HgCl<sub>2</sub> forms white or slate-coloured precipitate with stannous chloride.

$$2\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$$
White ppt.

 $\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \longrightarrow 2\text{Hg} + \text{SnCl}_4$ 
Grey ppt.

(iv) The solution of HgCl<sub>2</sub> with copper turning forms a grey deposit.

$$HgCl_2 + Cu \longrightarrow Hg + CuCl_2$$
  
Grey ppt.

#### Group II

When hydrogen sulphide is passed in acidified solution, the radicals of second group are precipitated as sulphides. The precipitate is treated with yellow ammonium sulphide. The sulphides of IIB are first oxidised to higher sulphides which then dissolve to form thio-compounds.

$$\begin{array}{c} \text{As}_2\text{S}_3 \ + \ 2(\text{NH}_4)_2\text{S}_2 \ \longrightarrow \ 2(\text{NH}_4)_2\text{S} \ + \ \text{As}_2\text{S}_5 \\ \text{Sb}_2\text{S}_3 \ + \ 2(\text{NH}_4)_2\text{S}_2 \ \longrightarrow \ 2(\text{NH}_4)_2\text{S} \ + \ \text{Sb}_2\text{S}_5 \\ \text{SnS} \ + \ (\text{NH}_4)_2\text{S}_2 \ \longrightarrow \ (\text{NH}_4)_2\text{S} \ + \ \text{SnS}_2 \\ \text{As}_2\text{S}_5 \ + \ 3(\text{NH}_4)_2\text{S} \ \longrightarrow \ 2(\text{NH}_4)_3\text{AsS}_4 \\ \text{Ammonium thioarsenate} \\ \text{Sb}_2\text{S}_5 \ + \ 3(\text{NH}_4)_2\text{S} \ \longrightarrow \ 2(\text{NH}_4)_3\text{SbS}_4 \\ \text{Ammonium thioantimonate} \\ \text{SnS}_2 \ + \ (\text{NH}_4)_2\text{S} \ \longrightarrow \ (\text{NH}_4)_2\text{SnS}_3 \\ \text{Ammonium thiostannate} \\ \end{array} \right\} \text{Soluble}$$

In case, the precipitate does not dissolve in yellow ammonium sulphide, it may be either HgS or PbS or  $Bi_2S_3$  or CuS or CdS. The precipitate is heated with dilute HNO<sub>3</sub>. Except HgS, all other sulphides of IIA are soluble.

$$3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO + 3S + 4H_2O$$
  
 $Bi_2S_3 + 8HNO_3 \longrightarrow 2Bi(NO_3)_3 + 2NO + 3S + 4H_2O$ 

$$3\text{CuS} + 8\text{HNO}_3 \longrightarrow 3\text{Cu(NO}_3)_2 + 2\text{NO} + 3\text{S} + 4\text{H}_2\text{O}$$
  
 $3\text{CdS} + 8\text{HNO}_3 \longrightarrow 3\text{Cd(NO}_3)_2 + 2\text{NO} + 3\text{S} + 4\text{H}_2\text{O}$ 

#### Hg<sup>2+</sup> (mercuric)

HgS is dissolved in aqua-regia.

$$3HgS + 2HNO_3 + 6HCl \longrightarrow 3HgCl_2 + 3S + 2NO + 4H_2O$$

The solution is divided into two parts:

**Part I:** Stannous chloride solution reduces HgCl<sub>2</sub> first into white Hg<sub>2</sub>Cl<sub>2</sub> and then to grey metallic mercury.

Part II: Copper displaces Hg from HgCl<sub>2</sub> which gets coated on copper turnings as a shining deposit.

#### Pb<sup>2+</sup> (lead)

In case the sulphide dissolves in dilute HNO<sub>3</sub>, a small part of the solution is taken. Dilute H<sub>2</sub>SO<sub>4</sub> is added. If lead is present, a white precipitate of lead sulphate appears.

$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow PbSO_4 + 2HNO_3$$
  
White ppt.

In absence of lead, the remaining solution is made alkaline by the addition of excess of NH<sub>4</sub>OH. Bismuth forms a white precipitate of Bi(OH)<sub>3</sub>, copper forms a deep blue coloured solution while cadmium forms a colourless soluble complex.

$$\begin{array}{c} \text{Bi(NO}_3)_3 + 3\text{NH}_4\text{OH} \longrightarrow & \text{Bi(OH)}_3 + 3\text{NH}_4\text{NO}_3 \\ & \text{White ppt.} \\ \text{Cu(NO}_3)_2 + 4\text{NH}_4\text{OH} \longrightarrow & [\text{Cu(NH}_3)_4](\text{NO}_3)_2 + 4\text{H}_2\text{O} \\ & \text{Tetrammine cupric nitrate} \\ & \text{(deep blue solution)} \end{array}$$

$$Cd(NO_3)_2 + 4NH_4OH \longrightarrow [Cd(NH_3)_4](NO_3)_2 + 4H_2O$$
Tetrammine cadmium nitrate (colourless solution)

#### Bi<sup>3+</sup> (bismuth)

The precipitate dissolves in dilute HCl.

$$Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O$$

**Part I:** Addition of excess of water to BiCl<sub>3</sub> solution gives a white precipitate due to hydrolysis.

$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$$
Bismuth
oxychloride
(White ppt.)

**Part II:** The solution of BiCl<sub>3</sub> is treated with sodium stannite solution when a black precipitate of metallic bismuth is formed.

$$2BiCl_3 + 3Na_2SnO_2 + 6NaOH \longrightarrow 3Na_2SnO_3 + 2Bi$$
  
Sod. stannite Sod. stannate  $+ 6NaCl + 3H_2O$ 

#### Cu<sup>2+</sup> (copper)

Blue coloured solution is acidified with acetic acid. When potassium ferrocyanide is added, a chocolate coloured precipitate is formed.

$$\begin{array}{c} \text{Cu(NH}_3)_4(\text{NO}_3)_2 + 4\text{CH}_3\text{COOH} \longrightarrow \text{Cu(NO}_3)_2 \\ + 4\text{CH}_3\text{COONH}_4 \\ 2\text{Cu(NO}_3)_2 + \text{K}_4[\text{Fe(CN)}_6] \longrightarrow \text{Cu}_2[\text{Fe(CN)}_6] + 4\text{KNO}_3 \\ & \text{Chocolate ppt.} \end{array}$$

#### Cd<sup>2+</sup> (cadmium)

H<sub>2</sub>S is passed through colourless solution. The appearance of yellow precipitate confirms the presence of cadmium.

$$Cd(NH_3)_4(NO_3)_2 + H_2S \longrightarrow CdS + 2NH_4NO_3 + 2NH_3$$
  
Yellow ppt.

#### 

In case the precipitate dissolves in yellow ammonium sulphide, the tests of the radicals arsenic, antimony and tin are performed. The sulphide is treated with concentrated hydrochloric acid. Antimony and tin sulphides dissolve while arsenic sulphide remains insoluble.

#### As<sup>3+</sup> (arsenic)

The insoluble sulphide is treated with concentrated nitric acid which is then heated with ammonium molybdate. Yellow precipitate of ammonium arsenomolybdate is formed.

$$(NH_4)_3AsO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O_4$$
  
Yellow ppt.

#### Sn<sup>2+</sup> or Sn<sup>4+</sup> (tin)

Solution of sulphide in concentrated HCl is reduced with iron fillings or granulated zinc.

$$SnS_2 + 4HCl \longrightarrow SnCl_4 + 2H_2S$$
  
 $SnCl_4 + Fe \longrightarrow SnCl_2 + FeCl_2$ 

HgCl<sub>2</sub> solution is added to above solution which gives first a white precipitate that turns to grey.

$$\begin{array}{ccc} 2 \text{HgCl}_2 + \text{SnCl}_2 & \longrightarrow & \text{Hg}_2 \text{Cl}_2 + \text{SnCl}_4 \\ & & \text{White ppt.} \\ \text{Hg}_2 \text{Cl}_2 + \text{SnCl}_2 & \longrightarrow & 2 \text{Hg} + \text{SnCl}_4 \\ & & & \text{Grev} \end{array}$$

#### Sb<sup>3+</sup>(antimony)

Filtrate of sulphide in concentrated HCl is divided into two parts:

**Part I:** On dilution with excess of water, a white precipitate of antimony oxychloride is obtained.

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$
White ppt.

**Part II :**  $H_2S$  is circulated. Orange precipitate is formed.  $2SbCl_3 + 3H_2S \longrightarrow Sb_2S_3 + 6HCl$ Orange ppt.

#### Group III

Hydroxides are precipitated on addition of excess of ammonium hydroxide in presence of ammonium chloride.

$$\begin{array}{c} AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3 + 3NH_4Cl \\ & Gelatinous \\ & ppt. \\ CrCl_3 + 3NH_4OH \longrightarrow Cr(OH)_3 + 3NH_4Cl \\ & Green ppt. \\ FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 + 3NH_4Cl \\ & Brownish \\ & red ppt. \end{array}$$

#### Fe<sup>3+</sup> (iron)

The brownish red precipitate dissolves in dilute HCl. The solution is divided into two parts:

**Part I :**  $K_4[Fe(CN)_6]$  solution is added which forms deep blue solution or precipitate.

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$$
Prussian blue

**Part II:** Addition of potassium thiocyanate solution gives a blood red colouration.

$$FeCl_3 + 3KCNS \longrightarrow Fe(CNS)_3 + 3KCl$$
Blood red colour

#### Cr<sup>3+</sup> (chromium)

The green precipitate is fused with fusion mixture  $(Na_2CO_3 + KNO_3)$ . The fused product is extracted with water or the precipitate is heated with NaOH and bromine water.

$$2\text{Cr}(\text{OH})_3 + 3\text{KNO}_3 + 2\text{Na}_2\text{CO}_3 \longrightarrow 2\text{Na}_2\text{CrO}_4 + 3\text{KNO}_2 \\ + 2\text{CO}_2 + 3\text{H}_2\text{O}$$
 or 
$$2\text{NaOH} + \text{Br}_2 \longrightarrow \text{NaBrO} + \text{NaBr} + \text{H}_2\text{O}$$
 
$$\text{NaBrO} \longrightarrow \text{NaBr} + [\text{O}]$$
 
$$2\text{Cr}(\text{OH})_3 + 4\text{NaOH} + 3[\text{O}] \longrightarrow 2\text{Na}_2\text{CrO}_4 + 5\text{H}_2\text{O}$$

The solution thus obtained contains sodium chromate. The solution is acidified with acetic acid and treated with lead acetate solution. A yellow precipitate appears.

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow PbCrO_4 + 2CH_3COONa$$
  
Yellow ppt.

#### Al<sup>3+</sup> (aluminium)

The gelatinous precipitate dissolves in NaOH.

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$
Soluble

The solution is boiled with ammonium chloride when Al(OH)<sub>3</sub> is again formed.

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow Al(OH)_3 + NaCl + NH_3$$

#### Group IV

On passing H<sub>2</sub>S through the filtrate of the third group, sulphides of fourth group are precipitated. NiS and CoS are black and insoluble in concentrated HCl while MnS (buff coloured), ZnS (colourless) are soluble in conc. HCl.

#### Zn<sup>2+</sup> (zinc)

The sulphide dissolves in HCl.

$$ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$$

When the solution is treated with NaOH, first a white precipitate appears which dissolves in excess of NaOH.

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$$

White ppt.

 $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$ 
(Soluble)

On passing H<sub>2</sub>S, white precipitate of zinc sulphide is formed.

$$Na_2ZnO_2 + H_2S \longrightarrow ZnS + 2NaOH$$
  
White ppt.

#### Mn<sup>2+</sup> (manganese)

Manganese sulphide dissolves in HCl.

$$MnS + 2HCl \longrightarrow MnCl_2 + H_2S$$

On heating the solution with NaOH and Br<sub>2</sub>-water, manganese dioxide gets precipitated.

$$MnCl_2 + 2NaOH \longrightarrow Mn(OH)_2 + 2NaCl$$
  
 $Mn(OH)_2 + O \longrightarrow MnO_2 + H_2O$ 

The precipitate is treated with excess of nitric acid and PbO<sub>2</sub> or Pb<sub>3</sub>O<sub>4</sub> (red lead). The contents are heated. The formation of permanganic acid imparts pink colour to the supernatant liquid.

$$2MnO_2 + 4HNO_3 \longrightarrow 2Mn(NO_3)_2 + 2H_2O + O_2$$
  
 $2Mn(NO_3)_2 + 5Pb_3O_4 + 26HNO_3 \longrightarrow 2HMnO_4$   
Permanganic acid (pink)  
 $+ 15Pb(NO_3)_2 + 12H_2O$ 

Note: The above test fails in presence of HCl.

#### Ni<sup>2+</sup> (nickel) and Co<sup>2+</sup> (cobalt)

The black precipitate is dissolved in aqua-regia.

$$3NiS + 6HCl + 2HNO_3 \longrightarrow 3NiCl_2 + 2NO + 3S + 4H_2O$$
  
 $3CoS + 6HCl + 2HNO_3 \longrightarrow 3CoCl_2 + 2NO + 3S + 4H_2O$ 

The solution is evaporated to dryness and residue extracted with dilute HCl. It is divided into three parts:

**Part I:** Add NH<sub>4</sub>OH (excess) and dimethyl glyoxime. A rosy red precipitate appears, if nickel is present.

$$\begin{array}{c|c} CH_3-C=NOH \\ NiCl_2+2 & | +2NH_4OH \longrightarrow \\ CH_3-C=NOH \\ OH & O \\ | & \uparrow \\ CH_3-C=N \\ | & N=C-CH_3 \\ | & +2NH_4Cl+2H_2O \\ | & N=C-CH_3 \\ | & O \end{array}$$

Part II: Add CH<sub>3</sub>COOH in excess and KNO<sub>2</sub>. The appearance of yellow precipitate confirms the presence of cobalt.

$$KNO_2 + CH_3COOH \longrightarrow CH_3COOK + HNO_2$$

$$CoCl_2 + 2KNO_2 \longrightarrow Co(NO_2)_2 + 2KCl$$

$$Co(NO_2)_2 + 2HNO_2 \longrightarrow Co(NO_2)_3 + NO + H_2O$$

$$Co(NO_2)_3 + 3KNO_2 \longrightarrow K_3[Co(NO_2)_6]$$

**Part III:** Solution containing either nickel or cobalt is treated with NaHCO<sub>3</sub> and bromine water. Appearance of apple green colour confirms the presence of cobalt. If no apple green colour is observed, the solution is heated when black precipitate is formed, which shows the presence of nickel.

$$\begin{array}{c} CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl \\ Co(HCO_3)_2 + 4NaHCO_3 \longrightarrow Na_4Co(CO_3)_3 + 3H_2O + 3CO_2 \\ Br_2 + H_2O \longrightarrow 2HBr + O \\ \\ 2Na_4Co(CO_3)_3 + H_2O + O \longrightarrow 2Na_3Co(CO_3)_3 + 2NaOH \\ Sod. \ cobalticarbonate \ (Green \ colouration) \\ NiCl_2 + 2NaHCO_3 \longrightarrow NiCO_3 + 2NaCl + H_2O + CO_2 \\ 2NiCO_3 + O \longrightarrow Ni_2O_3 + 2CO_2 \\ (Black) \end{array}$$

#### Group V

Ammonium carbonate precipitates V group radicals in the form of carbonates. These carbonates are soluble in acetic acid.

$$BaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ba + CO_2 + H_2O$$
  
 $SrCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Sr + CO_2 + H_2O$   
 $CaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + CO_2 + H_2O$ 

#### Ba<sup>2+</sup> (barium)

Barium chromate is insoluble and precipitated by the addition of potassium chromate solution.

$$Ba(CH_3COO)_2 + K_2CrO_4 \longrightarrow BaCrO_4 + 2CH_3COOK$$

#### Sr<sup>2+</sup> (strontium)

Strontium sulphate is insoluble and precipitated by the addition of ammonium sulphate solution.

$$\begin{array}{c} Sr(CH_3COO)_2 \ + \ (NH_4)_2SO_4 \longrightarrow SrSO_4 \ + \ 2CH_3COONH_4 \\ & White \ ppt. \end{array}$$

#### Ca<sup>2+</sup> (calcium)

Calcium oxalate is insoluble and precipitated by the addition of ammonium oxalate.

$$Ca(CH_3COO)_2 + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4 + 2CH_3COONH_4$$
 White ppt.

#### **Group VI**

In the filtrate of V-group, some quantity of ammonium oxalate is added as to remove Ba, Ca and Sr completely from the solution. The clear solution is concentrated and made alkaline with NH<sub>4</sub>OH. Disodium hydrogen phosphate is now added, a white precipitate is formed.

$$MgCl_2+Na_2HPO_4+NH_4OH \longrightarrow Mg(NH_4)PO_4+2NaCl+H_2O$$

Magnesium ammonium

phosphate

(White ppt.)

#### NH4 (ammonium)

The substance (salt or mixture) when heated with NaOH solution evolves ammonia.

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$$

When a rod dipped in HCl is brought on the mouth of the test-tube, white fumes of ammonium chloride are formed.

$$NH_3 + HCI \longrightarrow NH_4CI$$
White fumes

To the aqueous solution of ammonium salt when Nessler's reagents is added, brown coloured precipitate is formed.

$$2K_{2}HgI_{4} + NH_{4}Cl + 4KOH \longrightarrow Hg O + 7KI + KCl + 3H_{2}O$$

$$I$$

$$Iodide of Millon's base (Brown ppt.)$$

#### 18.6 DRY TESTS

Dry tests are of great importance as these tests give clear indications of the presence of certain radicals. The following tests are performed in dry state:

- (i) Flame test
- (ii) Borax bead test
- (iii) Microcosmic salt bead test
- (iv) Charcoal cavity test
- (v) Cobalt nitrate charcoal test

#### (i) Flame test

Some volatile salts impart characteristic colour to the non-luminous flame. The chlorides of the metals are more volatile in comparison to other salts. The metal chloride volatilises and its thermal ionisation takes place.

$$NaCl \implies Na^+ + Cl^-$$
  
 $CaCl_2 \implies Ca^{2+} + 2Cl^-$ 

The cations impart a characteristic colour to the flame as these absorb energy from the flame and transmit the same as light of characteristic colour.

**Procedure:** The platinum wire fused in a glass rod is heated in the flame till it imparts colourless flame. This is achieved by dipping the wire in conc. HCl and heating it. The process is repeated till it gives a colourless flame. The tip of the wire is now dipped in conc. HCl and then into the substance. The tip of the wire is strongly heated in the non-luminous flame and the colour of the flame is observed by the naked eye.

Colour of flame	Inference
<ol> <li>Golden yellow</li> </ol>	Sodium
2. Violet	Potassium
3. Brick red	Calcium
4. Crimson red	Strontium
5. Apple green	Barium
6. Green with a blue centre	Copper

Note: Flame test should not be performed in the presence of As, Sb, Bi, Sn and Pb as these radicals form alloy with platinum and hence, the wire is spoiled.

#### (ii) Borax bead test

On heating borax the colourless glassy bead formed consists of sodium metaborate and boric anhydride.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{Heat} Na_2B_4O_7 \xrightarrow{Heat} \underbrace{2NaBO_2 + B_2O_3}_{Glassy bead}$$

On heating with a coloured salt, the glassy bead forms a coloured metaborate in oxidising flame.

$$\begin{array}{c} CuSO_4 \longrightarrow CuO + SO_3 \\ CuO + B_2O_3 \longrightarrow Cu(BO_2)_2 \\ \hline Copper metaborate \\ \hline (Blue) \end{array}$$

The metaborates possess different characteristic colours. The shade of the colour gives a clue regarding the presence of the radical.

However, in reducing flame the colours may be different due to different reactions. For example, copper metaborate may be reduced to colourless cuprous metaborate or to metallic copper, which appears red and opaque.

$$2Cu(BO_2)_2 + C \longrightarrow 2CuBO_2 + B_2O_3 + CO$$
  
 $2Cu(BO_2)_2 + 2C \longrightarrow 2Cu + 2B_2O_3 + 2CO$ 

**Procedure:** The free end of a platinum wire is coiled into a small loop and heated in the Bunsen flame until red hot. It is dipped in borax and again heated, when borax swells up and then fused into a glassy bead.

The bead is moistened with water and dipped in the coloured salt. It is now heated first in the oxidising flame and then in the reducing flame and colours are noted in both the flames in hot and cold conditions.

	Colour of the bead in							
Metal	Oxidisin	g flame	Reducing flame					
	Hot Cold		Hot	Cold				
Copper	Green	Blue	Colourless	Brown-red				
Iron	Brown-yellow	Pale-yellow	Bottle green	Bottle green				
Chromium	Green	Green	Green	Green				
Cobalt	Blue	Blue	Blue	Blue				
Manganese	Violet	Amethyst red	Grey	Grey				
Nickel	Violet	Brown	Grey	Grey				

#### (iii) Microcosmic salt bead test

This test is similar to borax bead test. When microcosmic salt is heated, a colourless transparent bead of sodium metaphosphate is formed.

$$Na(NH_4)HPO_4 \longrightarrow NaPO_3 + NH_3 + H_2O$$
Sodium
metaphosphate

Sodium metaphosphate combines with metallic oxides to form orthophosphates which are usually coloured. The shade of the colour gives a clue regarding the presence of metal. Like borax bead test, colours are noted both in oxidising and reducing flames in hot and cold conditions.

	Colour of the bead in						
Metal	Oxidisin	g flame	Reducing flame				
	Hot Cold		Hot	Cold			
Copper	Green	Blue	Colourless	Red			
Iron	Yellow or	Yellow	Yellow	Colourless			
	reddish-brown						
Chromium	Green	Green	Green	Green			
Manganese	Violet	Violet	Colourless	Colourless			
Cobalt	Blue	Blue	Blue	Blue			
Nickel	Brown	Brown	-	Grey			

#### (iv) Charcoal cavity test

This test is carried out on a charcoal block in which a small cavity has been made by a knife. About 0.1 g of the substance is mixed with 0.2 g of anhydrous Na<sub>2</sub>CO<sub>3</sub> or fusion mixture and the mixture is placed in the cavity. The mass is moistened with a drop of water and heated in a reducing flame with the

blow pipe. The bead or incrustation formed is observed. When metallic salt is heated with Na<sub>2</sub>CO<sub>3</sub>, the metal carbonate is formed which decomposes into oxide. The carbon of the block reduces the oxide into metal. For example,

$$CuCl_2 + Na_2CO_3 \longrightarrow CuCO_3 + 2NaCl$$
 $CuCO_3 \longrightarrow CuO + CO_2$ 
 $CuO + C \longrightarrow Cu + CO$ 

Observation	Inference
1. Formation of metallic bead :	
(a) Lustrous white, malleable	Ag
(b) Greyish white, marks paper	Pb
(c) White, does not mark paper	Sn
(d) Red	Cu
2. Incrustation with metal:	
(a) White incrustation, brittle metal	Sb
(b) Yellow incrustation, brittle metal	Bi
(c) Yellow incrustation, malleable metal	Pb
3. Incrustation without metal:	
(a) White and yellow when hot	ZnO, SnO
(b) Yellow and orange when hot	BiO
(c) Brown	CdO
(d) White (volatile, garlic odour)	As <sub>2</sub> O <sub>3</sub>

#### (v) Cobalt nitrate charcoal test

A small amount of the substance and twice its bulk of sodium carbonate is placed in the charcoal cavity. A drop of water is added and the mass is heated in an oxidising flame with the help of blow pipe. After cooling, one or two drops of cobalt nitrate solution are added and the mass is again heated in the oxidising flame. The colour produced in the cavity is noted.

By heating the salt with sodium carbonate, the oxide is formed which on heating with cobalt nitrate form a mixed oxide of a characteristic colour.

$$ZnSO_4 + Na_2CO_3 \longrightarrow ZnCO_3 + Na_2SO_4$$
 $ZnCO_3 \longrightarrow ZnO + CO_2$ 
 $2Co(NO_3)_2 \longrightarrow 2CoO + 4NO_2 + O_2$ 
 $ZnO + CoO \longrightarrow CoZnO_2$ 
Rinnmann green

Observation	Inference
(a) Blue mass	Aluminium
(b) Green residue	Zinc
(c) Pink residue	Magnesium
(d) Bluish-green	- Tin

### 50ME-50LVED-PROBLEMS

**Problem 1.** Two solid laboratory reagents 'A' and 'B' give the following reactions:

#### Compound A:

- (i) On strongly heating it gives two oxides of sulphur.
- (ii) On adding aqueous NaOH solution to its aqueous solution a dirty green precipitate is obtained, which starts turning brown on exposure to air.

#### Compound B:

- (iii) It imparts green colour to the flame.
- (iv) Its solution does not give a precipitate on passing  $H_2S$ .
- (v) When it is heated with solid  $K_2Cr_2O_7$  and concentrated  $H_2SO_4$ , a red gas is evolved. The gas when passed in an aqueous solution of NaOH, turns it yellow.

Identify 'A' and 'B'.

[Roorkee 1993]

#### **Solution:**

**Compound A:** (i) Compound 'A' is ferrous sulphate which gives  $SO_2$  and  $SO_3$  on heating.

(ii) Ferrous sulphate gives dirty green Fe(OH)<sub>2</sub> with aqueous NaOH.

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$
(Dirty green)

Fe(OH)<sub>2</sub> turns brown on oxidation, when exposed to atmosphere.

$$2\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \longrightarrow 2\text{Fe}(\text{OH})_3$$
Brown

**Compound B:** (iii) and (iv) Compound 'B' is  $BaCl_2$  which imparts green colour to flame and does not give any precipitate with  $H_2S$ .

(v)  $BaCl_2$  forms chromyl chloride, when treated with  $K_2Cr_2O_7$  and conc.  $H_2SO_4$ .

$$2BaCl_2 + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow$$

$$K_2SO_4 + 2BaSO_4 + 2CrO_2Cl_2 + 3H_2O$$
  
Chromyl chloride

(Red gas)

Chromyl chloride forms, yellow coloured Na<sub>2</sub>CrO<sub>4</sub> with aqueous NaOH.

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$
Yellow
(Sodium chromate)

**Problem 2.** A light green crystalline compound responds to the following test:

- (i) Its aqueous solution gives a brown precipitate or colouration with alkaline  $K_2HgI_4$  solution.
- (ii) Its aqueous solution gives a blue colour with  $K_3Fe(CN)_6$  solution.
- (iii) Its solution in hydrochloric acid gives a white precipitate with BaCl<sub>2</sub> solution. Identify the ions present and suggest the formula of the compound. [J.I.T. 1992]

#### **Solution:**

- (i) K<sub>2</sub>HgI<sub>4</sub> is called Nessler's reagent. It is specially used to check the presence of NH<sub>4</sub><sup>+</sup>; giving brown precipitate. Hence, compound contains NH<sub>4</sub><sup>+</sup> ion.
- (ii) With K<sub>3</sub>Fe(CN)<sub>6</sub>, only Fe<sup>2+</sup> ion gives blue colour called Turnbull's blue.
- (iii) BaCl<sub>2</sub> gives white precipitate with  $SO_4^{2-}$  ions. Hence, compound (X) would be Mohr's salt. FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O which contains all the three ions.

**Problem 3.** An aqueous solution of gas (X) shows the following reactions:

- (i) It turns red litmus blue.
- (ii) When added in excess to a copper sulphate solution, a deep blue colour is obtained.
- (iii) On addition of FeCl<sub>3</sub> solution, a brown precipitate, soluble in dilute  $HNO_3$  is obtained. Identify (X) and give equations for the reactions at step (ii) and (iii).

Roorkee 1991]

#### **Solution:**

Gas 'X' is soluble in water forming basic solution because it turns red litmus blue. Hence, the gas may be NH<sub>3</sub>.

$$NH_3 + H_2O \longrightarrow NH_4OH$$
 $CuSO_4 + 4NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$ 
(Tetraamine cupric sulphate)
Deep blue complex

Ferric chloride gives brown precipitate of Fe(OH)<sub>3</sub>.

 $FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 + 3NH_4Cl$ (Brown precipitate)

Brown precipitate is soluble in HNO<sub>3</sub>.

**Problem 4.** A certain compound (X) is used in laboratory for analysis, its aqueous solution gives the following reactions:

- (i) On adding copper sulphate, a brown precipitate is obtained which turns white on addition of excess of  $Na_2S_2O_3$  solution.
- (ii) On addition of  $Ag^+$  ion solution a yellow curdy precipitate is obtained which is insoluble in ammonium hydroxide.

Identify (X) and give equations for the reactions at step (i) and (ii). [Roorkee 1991]

#### **Solution:**

Yellow curdy precipitate with Ag<sup>+</sup> confirms the presence of I<sup>-</sup> ion in the compound. The precipitate is insoluble in NH<sub>4</sub>OH.

$$Ag^+ + I^- \longrightarrow AgI$$

Compound (X) gives brown precipitate with CuSO<sub>4</sub> which becomes white when Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is added. Thus, compound (X) should be KI. Reactions involved may be given as:

$$\begin{array}{c} \text{CuSO}_4 + 2\text{KI} & \longrightarrow & \text{CuI}_2 + \text{K}_2\text{SO}_4 \\ 2\text{CuI}_2 & \longrightarrow & \text{Cu}_2\text{I}_2 & + \text{I}_2 \\ & \text{White} & \text{Brown} \\ & & & & & & \\ (\text{Insoluble}) & \\ 2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 & \longrightarrow & \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$$

After removal of iodine, white precipitate of  $Cu_2I_2$  appears as both  $Na_2S_4O_6$  and NaI form colourless solution.

**Problem 5.** A compound on heating with an excess of caustic soda solution liberates a gas (B) which gives white fumes on exposure of HCl. Heating it continued to expel the gas completely. The resultant alkaline solution again liberates the same gas (B) when heated with zinc powder. However the compound (A), when heated alone does not give nitrogen. Identify (A) and (B).

#### **Solution:**

Gas (B) gives white fumes with HCl, hence it should be NH<sub>3</sub>. Thus, compound (A) must be an ammonium salt.

We know that nitrates and nitrites on heating with Zn and alkali liberate NH<sub>3</sub> gas. Hence, the compound (A) should be ammonium nitrate or nitrite. But compound (A) does not give N<sub>2</sub> on heating, hence it may not be ammonium nitrite.

#### Reactions involved:

$$NH_4NO_3 + NaOH \longrightarrow NaNO_3 + H_2O + NH_3 \uparrow$$
 $(A)$ 
 $NH_3 + HCl \longrightarrow NH_4Cl$ 
 $(White fumes)$ 
 $NaNO_3 + 8[H] \xrightarrow{Zn/NaOH} NaOH + 2H_2O + NH_3 \uparrow$ 

**Problem 6.** An unknown solid mixture contains one or two of the following: CaCO<sub>3</sub>, BaCl<sub>2</sub>, AgNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, ZnSO<sub>4</sub> and NaOH. The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When dilute hydrochloric acid is gradually added to above solution, a precipitate is formed which dissolves with further addition of the acid. What is/are present in the solid?

Give equations to explain the appearance of the precipitate—and its dissolution.

#### **Solution:**

- (i) Mixture gives pink colour with phenolphthalein, hence it should contain NaOH.
- (ii) Aqueous solution gives precipitate with dil. HCl which dissolves in excess HCl. It means that compound is zinc salt.

Thus, the mixture should be of NaOH and ZnSO<sub>4</sub>. Reactions involved may be given as:

$$ZnSO_4 + 4NaOH \longrightarrow Na_2ZnO_2 + Na_2SO_4 + 2H_2O$$
Sodium zincate
 $Na_2ZnO_2 + 2HCl \longrightarrow 2NaCl + Zn(OH)_2 \downarrow$ 
White ppt.

 $Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + 2H_2O$ 
Soluble

Hence, NaOH and ZnSO<sub>4</sub> are present in the solid.

**Problem 7.** The gas liberated on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of  $K_2HgI_4$ . The aqueous solution of mixture on treatment with  $BaCl_2$  gives a white precipitate which is sparingly soluble in conc. HCl. On heating the mixture with  $K_2Cr_2O_7$  and conc.  $H_2SO_4$ , red vapours (A) are produced. The aqueous solution of mixture gives a deep blue calouration (B) with potassium ferricyanide. Identify the radicals in given mixture and write the balanced equation for formation of (A) and (B). [I.I.T. 1991]

#### **Solution:**

- (i) Gas given by heating mixture with NaOH gives brown ppt. with Nessler's reagent K<sub>2</sub>HgI<sub>4</sub>. It shows that the salt is a ammonium salt.
- (ii) BaCl<sub>2</sub> solution gives white precipitate sparingly soluble in HCl. It shows the presence of  $SO_4^2$  ion in the mixture.
- (iii) Blue colour with  $K_3Fe(CN)_6$  indicates the presence of  $Fe^{2+}$  ion.

(iv) Mixture + 
$$K_2Cr_2O_7 \xrightarrow{H_2SO_4} Red vapours (CrO_2Cl_2)$$
(A)

It shows that the mixture contains Cl<sup>-</sup> ion. Reactions involved may be given as:

(i) 
$$NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + NH_3 \uparrow + H_2O$$
  
 $K_2HgI_4 + NaOH + NH_3 \rightarrow O \xrightarrow{Hg} NH_2I + KI + H_2O + NaI$   
(Brown ppt.)

(ii) 
$$FeSO_4 + BaCl_2 \longrightarrow BaSO_4 + FeCl_2$$
(White ppt.)

(iii) 
$$3\text{FeSO}_4 + 2\text{K}_3\text{Fe}(\text{CN})_6 \longrightarrow 3\text{K}_2\text{SO}_4 + \text{Fe}_3[\text{Fe}(\text{CN})_6]_2$$
  
Ferrous ferricyanide (Blue)

(iv) 
$$4NH_4Cl + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow 2CrO_2Cl_2 + K_2SO_4$$
  
Chromyl chloride  $+ 3H_2O + 2(NH_4)_2SO_4$ 

**Problem 8.** A colourless solid (A) liberates a brown gas (B) on acidification, a colourless alkaline gas (C) on treatment with NaOH, and a colourless non-reactive gas (D) on heating. If heating of the solid continued, it completely disappears. Identify (A) to (D).

#### Solution:

Alkaline gas (C) with NaOH indicate that solid should be ammonium salt. Heating the salt, a colourless gas (D) non-reactive is formed. The gas (D) may be nitrogen. The compound may thus be NH<sub>4</sub>NO<sub>2</sub>. Reactions involved may be given as:

(i) 
$$NH_4NO_2 \xrightarrow{HCl} NH_4Cl + HNO_2$$

$$(A) \qquad \qquad 2HNO_2 \longrightarrow H_2O + 2NO + [O]$$

$$2NO + 2[O] \longrightarrow 2NO_2$$

$$(B) Brown gas$$

(ii) 
$$NH_4NO_2 + NaOH \longrightarrow NaNO_2 + H_2O + NH_3 \uparrow$$
(C)

(iii) 
$$NH_4NO_2 \xrightarrow{\text{Heat}} N_2 \uparrow + 2H_2O \uparrow$$
(A) (D)

**Problem 9.** An aqueous solution of gas (X) gives the following reactions:

- (i) It decolourizes an acidified  $K_2Cr_2O_7$  solution.
- (ii) On boiling it with  $H_2O_2$ , cooling it and then adding an aqueous solution of  $BaCl_2$  a precipitate insoluble in dil. HCl is obtained.
- (iii) On passing  $H_2S$  in the solution, a white turbidity is obtained.

Identify (X) and give equations for the reactions at steps (i), (ii) and (iii). [Roorkee 1990]

#### Solution:

The reactions given in (i), (ii) and (iii) may be explained if we consider the gas (X) to be  $SO_2$ .

(i) 
$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

(ii) 
$$H_2O + SO_2 + [O] \longrightarrow H_2SO_4$$
  
 $H_2O_2 + SO_2 \longrightarrow H_2SO_4$   
 $H_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2HCl$   
(White ppt.)

**Problem 10.** A black coloured compound (A) on reaction with dil.  $H_2SO_4$  gives a gas (B) which on passing in a solution of an acid (C) gives a white turbidity (D). Gas (B) when passed in acidified solution of (E) gives a precipitate (F) soluble in dilute HNO3. After boiling this solution when excess of  $NH_4OH$  is added, a blue coloured compound (G) is formed. To this solution on addition of acetic acid and aqueous potassium ferrocyanide a chocolate coloured precipitate (H) is obtained. On addition of an aqueous solution of  $BaCl_2$  to an aqueous solution of (E), a white precipitate insoluble in  $HNO_3$  is obtained. Identify (A) to (H). [Roorkee 1987]

#### Solution:

Flow diagram of the reaction may be given as:

$$A \text{ [Black]} \xrightarrow{\text{H}_2\text{SO}_4} B \text{ (gas)} \xrightarrow{\text{Acid}} \text{Turbidity } (D)$$

$$A \text{ (ad soln. of } (E)$$

$$\downarrow \qquad \qquad \qquad \downarrow \qquad$$

E (aqueous solution)  $\xrightarrow{\operatorname{BaCl}_2}$  White precipitate insoluble in

HNO<sub>3</sub>

#### Reactions involved may be given as:

FeS + 
$$H_2SO_4 \longrightarrow FeSO_4 + H_2S$$
Ferrous sulphide
Black (A)

 $H_2S + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + S \uparrow$ 
(B)
(C)
Colloidal sulphur
(D) (Turbid)

$$CuSO_4 + H_2S \xrightarrow{HCl} CuS + H_2SO_4$$
Precipitate
(F)

 $3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$ 
(F)

$$Cu(NO_3)_2 + H_2SO_4 \longrightarrow CuSO_4 + 2HNO_3$$

$$CuSO_4 + 4NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$$
(Deep blue)
(G)

$$[Cu(NH_3)_4]SO_4 + 4CH_3COOH \longrightarrow CuSO_4 + 4CH_3COONH_4$$

$$\begin{array}{c} CuSO_4 + BaCl_2 \longrightarrow & BaSO_4 + CuCl_2 \\ & \text{White ppt.} \\ & \text{insoluble in HNO}_3 \end{array}$$

$$2\text{CuSO}_4 + \text{K}_4\text{Fe}(\text{CN})_6 \longrightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] + 2\text{K}_2\text{SO}_4$$
Cupric ferrocyanide
(Chocolate precipitate)

**Problem 11.** Give the complete balanced equation for the following:

- (i) Mercurous nitrate reacts with excess KI solution.
- (ii) Sodium chromite solution reacts with  $H_2O_2$  in presence of NaOH.
- (iii) Nickel sulphate reacts with dimethyl glyoxime reagent in ammonical solution. [M.L.N.R. 1997]

#### **Solution:**

(i) 
$$Hg_2(NO_3)_2 + 2KI \longrightarrow Hg_2I_2 + 2KNO_3$$
  
 $Hg_2I_2 + 2KI \longrightarrow K_2HgI_4 + Hg$ 

(ii) 
$$Na_2CrO_2 + 2H_2O_2 \longrightarrow Na_2CrO_4 + H_2O$$

(iii) NiSO<sub>4</sub> + 2 
$$CH_3$$
—C=NOH  $+ 2NH_4OH \longrightarrow CH_3$ —C=NOH

**Problem 12.** (i) The yellow coloured precipitate of compound (A) is formed on passing  $H_2S$  through a neutral solution of salt (B).

- (ii) (A) is soluble in hot dilute  $HNO_3$  but insoluble in yellow ammonium sulphide.
- (iii) The solution of (B) on treatment with small quantity of  $NH_3$  gives white precipitate which becomes soluble in excess of it forming a compound (C).

- (iv) The solution of (B) gives white precipitate with small concentration of KCN which becomes soluble in excess of this reagent forming a compound (D).
  - (v) The solution of (D) on treatment with  $H_2S$  gives (A).
- (vi) The solution of (B) in dil. HCl on treatment with a solution of BaCl<sub>2</sub> gives white precipitate of compound (E) which is insoluble in conc. HNO<sub>3</sub>.

Identify (A) to (E) and give chemical equations for the reactions at steps (i) to (iii) to (vi). [Roorker 1998]

#### Solution:

Yellow precipitate of CdS is (A).

(i) 
$$CdSO_4 + H_2S \longrightarrow CdS + H_2SO_4$$
(B)  $(A)$ 

(ii) 
$$CdS + 2HNO_3 \longrightarrow Cd(NO_3)_2 + H_2S$$
  
Soluble

CdS - Insoluble in yellow ammonium sulphide.

$$CdSO_4 + 2NH_4OH \longrightarrow Cd(OH)_2 + (NH_4)_2SO_4$$

(iii) 
$$Cd(OH)_2 + 4NH_4OH \longrightarrow [Cd(NH_3)_4](OH)_2 + 4H_2O$$

(iv) 
$$CdSO_4 + 2KCN \longrightarrow Cd(CN)_2 + K_2SO_4$$

$$\frac{White}{Cd(CN)_2 + 2KCN \longrightarrow K_2[Cd(CN)_4]}$$
(D) Soluble

(v) 
$$K_2[Cd(CN)_4] + H_2S \longrightarrow CdS + 2KCN + 2HCN$$

(vi) 
$$CdSO_4 + BaCl_2 \longrightarrow BaSO_4 + CdCl_2$$
(E)

White precipitate insoluble in HNO<sub>3</sub>.

**Problem 13.** (i) An aqueous solution of a compound (A) is acidic towards litmus and (A) is sublimed at about 300°C.

- (ii) (A) on treatment with an excess of NH<sub>4</sub>SCN gives a red coloured compound (B) and on treatment with a solution of  $K_4[Fe(CN)_6]$  gives a blue coloured compound (C).
- (iii) (A) on heating with excess of  $K_2Cr_2O_7$  in presence of concentrated  $H_2SO_4$  evolves deep red vapours of (D).
- (iv) On passing the vapours of (D) into a solution of NaOH and then adding the solutions of acetic acid and lead acetate, a yellow precipitate of compound (E) is obtained.

Identify (A) to (E) and give chemical equations for the reactions at steps (ii) to (iv). [Roorkee 1998]

#### **Solution:**

(i) 
$$\operatorname{FeCl}_3 + 3H_2O \longrightarrow \operatorname{Fe}(OH)_3 + 3HCl$$

Solution becomes acidic due to hydrolysis. FeCl<sub>3</sub> sublimes at 300°C.

(ii) 
$$FeCl_3 + 3NH_4SCN \longrightarrow Fe(CNS)_3 + 3NH_4Cl$$
(B) Blood red

$$4\text{FeCl}_3 + 3\text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl}_6(C)$$
 Prussian blue

(iii) 
$$4\text{FeCl}_3 + 9\text{H}_2\text{SO}_4 + 3\text{K}_2\text{Cr}_2\text{O}_7 \longrightarrow 6\text{CrO}_2\text{Cl}_2 + 2\text{Fe}_2(\text{SO}_4)_3 + 3\text{K}_2\text{SO}_4 + 9\text{H}_2\text{O}_4$$

(D)

Chromyl chloride

(iv) 
$$CrO_2Cl_2 + 4NaOH \longrightarrow 2NaCl + Na_2CrO_4 + 2H_2O$$
  
 $Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4 + 2CH_3COONa$   
(E) Yellow ppt.

**Problem 14.** (i) A powdered substance (A) on treatment with fusion mixture gives a green coloured compound (B).

- (ii) The solution of (B) in boiling water on acidification with dilute  $H_2SO_4$  gives a pink coloured compound (C).
- (iii) The aqueous solution of (A) on treatment with excess of NaOH and bromine water gives a compound (D).
- (iv) A solution of (D) in conc.  $HNO_3$  on treatment with lead peroxide at boiling temperature produced a compound (E) which was of the same colour as that of (C).
- (v) A solution of (A) in dilute HCl on treatment with a solution of barium chloride gave a white precipitate of compound (F) which was insoluble in conc. HNO<sub>3</sub> and conc. HCl

Identify (A) to (F) and give balanced chemical equations for the reactions at steps (i) to (v). [Roorkee 2001]

#### Solution:

The compound (A) is a sulphate as its solution in dilute HCl on treatment with barium chloride solution gives a white precipitate of barium sulphate (F) which is insoluble in conc. HNO<sub>3</sub> and conc. HCl.

Solution of (A) in dilute 
$$HCl + BaCl_2 \longrightarrow BaSO_4$$
 (White ppt.)

(F)

Insoluble in conc.  $HNO_3$  and conc.  $HCl$ 

From reactions (i) and (ii), it is clear that the compound (A) is manganese sulphate.

(i) MnSO<sub>4</sub> + 
$$2Na_2CO_3 + 2KNO_3$$
  $\longrightarrow Na_2MnO_4$ 
(B)
Green coloured compound

+  $2KNO_2 + Na_2SO_4 + 2CO_2$ 
(ii)  $3Na_2MnO_4 + 2H_2SO_4 \longrightarrow 2NaMnO_4 + 2Na_2SO_4$ 
(B)
(C)
Pink coloured compound

+  $MnO_2 + 2H_2O_4$ 
(iii)  $MnSO_4 + 4NaOH + Br_2 \longrightarrow MnO_2 + Na_2SO_4$ 
(D)
+  $2NaBr + 2H_2O_4$ 
(iv)  $2MnO_2 + 10HNO_3 + 5PbO_2 \longrightarrow 2HMnO_4$ 

solution  

$$+ 5Pb(NO_3)_2 + 4H_2O + O_2$$
  
(v) MnSO<sub>4</sub> + BaCl<sub>2</sub>  $\longrightarrow$  BaSO<sub>4</sub> + MnCl<sub>2</sub>  
(F)

White ppt.

Pink coloured

**Problem 15.** A white substance (A) reacts with dilute  $H_2SO_4$  to produce a colourless gas (B) and a colourless

solution (C). The reaction between (B) and acidified  $K_2Cr_2O_7$  solution produces a green solution and a slightly coloured precipitate (D). The substance (D) burns in air to produce a gas (E) which reacts with (B) to yield (D) and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH<sub>3</sub> or NaOH to (C) produces first a precipitate, which dissolves in the excess of respective reagent to produce a clear solution in each case. Identify (A), (B), (C), (D) and (E) write the equations of the reactions involved.

#### Solution:

The white substance (A) is ZnS.

 $S + O_2 \longrightarrow SO_2$ 

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$

$$(E) \quad (B) \quad (D) \quad Colourless \ liquid$$

$$CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O$$

$$White \quad Blue$$

$$(Anhydrous)$$

$$ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2 + Na_2SO_4$$

$$(C) \quad White \quad Fpt.$$

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$$
Soluble in water

$$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)_2SO_4$$

$$Zn(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \rightarrow [Zn(NH_3)_4]SO_4 + 4H_2O$$
Soluble complex (Clear solution)

**Problem 16.** When a crystalline compound 'X' is heated with  $K_2Cr_2O_7$  and concentrated  $H_2SO_4$ , a reddish brown gas 'A' is evolved. On passing 'A' into caustic soda, an yellow coloured solution of 'B' is obtained. Neutralizing the solution of 'B' with acetic acid and on subsequent addition of lead acetate, an yellow precipitate of 'C' is obtained. When 'X' is heated with NaOH, a colourless gas is evolved and on passing this gas into  $K_2HgI_4$  solution, a reddish brown precipitate 'D' is formed. Identify 'A', 'B', 'C', 'D' and 'X'. Write the equation of reactions involved.

#### **Solution:**

The given information in the question infer that compound 'X' will be NH<sub>4</sub>Cl.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$$
  
 $NH_4Cl + H_2SO_4 \longrightarrow NH_4HSO_4 + HCl$ 

$$CrO_{3} + 2HCl \longrightarrow CrO_{2}Cl_{2} + H_{2}O$$

$$(A)$$

$$Reddish brown gas$$

$$CrO_{2}Cl_{2} + 4NaOH \longrightarrow Na_{2}CrO_{4} + 2NaCl + 2H_{2}O$$

$$(B)$$

$$Yellow coloured solution$$

$$Na_{2}CrO_{4} + (CH_{3}COO)_{2}Pb \xrightarrow{CH_{3}COOH}$$

$$PbCrO_{4} + 2CH_{3}COONa$$

$$(C)$$

$$(Yellow precipitate)$$

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$$
Colourless gas

 $NH_2$ 
 $NH_3 + 2K_2HgI_4 + H_2O \longrightarrow Hg \longrightarrow Hg$ 
 $Hg \longrightarrow O$ 
 $Hg$ 

(Brown precipitate)

### - • • • - PRACTICE PROBLEMS

### PROBLEMS - • • • -

#### ■ Subjective Type Questions

- 1. What do you mean by inorganic mixture analysis and what do you do in it?
- 2. What are acidic and basic radicals? Or What are anions and cations?
- 3. Name the acid radicals detected with dilute H<sub>2</sub>SO<sub>4</sub>.
- 4. Name the acid radicals detected with concentrated H<sub>2</sub>SO<sub>4</sub>.
- 5. What is sodium carbonate extract? What is its utility in qualitative analysis?
- **6.** How will you test carbonate in a mixture? Can you test carbonate in presence of sulphite?
- 7. Is there any gas other than  $CO_2$  which turns lime water milky?
- **8.** How will you test sulphide in a mixture?
- **9.** What is chromyl chloride test? Explain it with reactions.
- 10. Name the brown gas evolved in the test of nitrate ion. How is this ion confirmed?
- 11. How will you detect bromide or iodide by chloroform layer test?
- 12. How will you detect oxalate in a mixture?
- 13. What is ring test? Explain it.
- 14. Name the acidic radicals that are detected when concentrated H<sub>2</sub>SO<sub>4</sub> is used alongwith:
  - (a) Copper turnings (b) Potassium dichromate (c) Ethyl alcohol.
- **15.** How will you test phost hate in a mixture? Is there any other radical which corresponds to this test?
- **16.** Why is original solution prepared for the identification of basic radicals? Why are HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> generally not used for the preparation of an original solution?
- 17. What is a group reagent? Name the group reagents for second, third and fourth groups of mixture analysis.
- 18. Name the three chlorides which are insoluble in dilute HCl. Name one chloride, which is soluble in hot water but insoluble in cold water.
- 19. Sometimes, a white precipitate is obtained even in the absence of members of 1st group on the addition of HCl. Explain it.
- 20. Why does Hg<sub>2</sub>Cl<sub>2</sub> turn black on the addition of NH<sub>4</sub>OH?
- 21. State how the following substances may be dissolved? PbSO<sub>4</sub>; AgCl; BaSO<sub>4</sub>; HgS.

- 22. Give examples and explain with equations:
  - (a) Two colourless solutions give a black precipitate on mixing.

(Iodide of Millon's base)

- (b) Two colourless solutions give a red precipitate on mixing, soluble in excess of one of them.
- (c) Two colourless solutions give a white precipitate on mixing, soluble in ammonium hydroxide.
- (d) Two colourless solutions give a yellow precipitate on mixing.
- 23. Why are the members of IV group not precipitated in II group although H<sub>2</sub>S is group reagent in both?
- 24. What is yellow ammonium sulphide? Why is yellow ammonium sulphide and not ordinary ammonium sulphide used for the separation of IIA and IIB sub-groups?
- 25. For the analysis of basic radicals of group II, H<sub>2</sub>S is passed in acidic medium, while for the basic radicals of group IV, in alkaline medium, why so?
- **26.** Explain, while performing qualitative analysis of basic radicals of third group, why ammonium chloride is added in excess before adding ammonium hydroxide?
- 27. How is copper tested? What is the chocolate precipitate obtained in the test of copper?
- 28. Name the two sulphides which are yellow in colour. How will you test the basic radicals present in them?
- 29. What happens when?
  - (a) Copper sulphate is treated with excess of NH<sub>4</sub>OH.
  - (b) Bismuth chloride is treated with sodium stannite solution in presence of NaOH.
  - (c) Stannous chloride is treated with mercuric chloride.
  - (d) Excess of water is added to concentrated solution of antimony chloride.
- **30.** (a) What is the function of concentrated HNO<sub>3</sub> in third group?
  - (b) Will you add HNO<sub>3</sub> in third group even if iron is given in ferric state in the mixture?
  - (c) Can you use NaCl and NaOH instead of NH<sub>4</sub>Cl and NH<sub>4</sub>OH in third group?
- 31. (a) How will you test for iron?
  - (b) What is the yellow precipitate obtained in the test of chromium?
  - (c) Which hydroxide dissolves in NaOH? Give equation. (i) Fe(OH)<sub>3</sub> (ii) Cu(OH)<sub>3</sub> (iii) Al(OH)<sub>3</sub>.

- **32.** What is the colour of nickel sulphide? How is nickel tested by dimethyl glyoxime?
- 33. What is the group reagent of V group? Why is it necessary to test for V group radicals in the order of Ba<sup>2+</sup>, Sr<sup>2+</sup> and Ca<sup>2+</sup> only?
- **34.** What is the white precipitate obtained in the test of magnesium?
- 35. How will you test zinc ion and mercuric ion in the laboratory?
- **36.** Give the chemistry of flame test. What colour is obtained in the test of calcium and barium salts?
- **37.** How is borax bead test performed? Give the chemistry of this test.
- 38. An aqueous solution of salt (A) gives a white precipitate (B) with NaCl solution. The filtrate gives a black precipitate, (C) when H<sub>2</sub>S is passed into it. Compound (B) dissolves in hot water and the solution gives a yellow precipitate (D) on treatment with sodium iodide and cooling. The compound (A) does not give any gas with dilute HCl but liberates a reddish-brown gas on heating. Identify the compounds (A) to (D).

[Hint: Since the crystalline substance (B) dissolves in hot water and gives a yellow precipitate with NaI, it should be lead chloride (PbCl<sub>2</sub>) and the solution (A) consists a lead salt.

$$\begin{array}{c} \operatorname{PbCl_2} + \operatorname{2NaI} \longrightarrow & \operatorname{PbI_2} + \operatorname{2NaCl} \\ \text{(B)} & \operatorname{Yeilow} \\ \text{(D)} \end{array}$$

The compound (A) does not give any gas with dilute HCl but liberates a reddish-brown gas on heating, it should be lead nitrate, Pb(NO<sub>2</sub>)<sub>2</sub>.

$$\begin{array}{ccc} \text{Pb}(\text{NO}_3)_2 & \longrightarrow & \text{PbO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \\ & & \text{Reddish-brown gas} \end{array}$$

Lead chloride is sparingly soluble in water. When H<sub>2</sub>S is passed, it gives a black precipitate of lead sulphide, PbS.

$$PbCl_2 + H_2S \longrightarrow PbS + 2HCl$$
Black ppt.
(C)

Thus, (A) is lead nitrate,  $Pb(NO_3)_2$ ;

(B) is lead chloride, PbCl<sub>2</sub>;

(C) is lead sulphide, PbS;

and (D) is lead iodide, PbI<sub>2</sub>.]

39. A mixture of two salts was treated as follows:

- (i) The mixture was heated with manganese dioxide and concentrated H<sub>2</sub>SO<sub>4</sub>, when yellowish green gas was liberated.
- (ii) The mixture on heating with NaOH solution gave a gas which turned red litmus blue.
- (iii) Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with NH<sub>4</sub>CNS.
- (iv) The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of K<sub>2</sub>HgI<sub>4</sub> to give brown precipitate.

Identify the two salts. Give ionic reactions involved in the tests (i), (ii) and (iii). [LI.T. 1987]

[**Hint**: Tests (ii) and (iv) show the presence of ammonium radical.

Test (i) shows the presence of Cl<sup>-</sup> ion and test (iii) shows the presence of Fe<sup>2+</sup> and Fe<sup>3+</sup> ion.

$$2Cl^- + MnO_2 + H_2SO_4 + 2H^+ \longrightarrow MnSO_4 + 2H_2O + Cl_2$$
 (Yellowish green) 
$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$$

NH<sub>3</sub> turns red litmus blue  

$$3Fe^{2^+} + 2[Fe(CN)_6]^{3^-} \longrightarrow Fe_3[Fe(CN)_6]_2$$
(Blue ppt.)  
 $Fe^{3^+} + 3CNS^- \longrightarrow Fe(CNS)_3$ 
(Blood red colour)

Thus, the mixture consists FeCl<sub>2</sub> and NH<sub>4</sub>Cl. Some of the FeCl<sub>2</sub> has undergone oxidation into FeCl<sub>3</sub> with atmospheric oxygen.]

- 40. Identify the unknown species and complete the following:
  - (i)  $(A) + BaCl_2 \longrightarrow White precipitate$
  - (ii) NaOH +  $(B) \longrightarrow NH_3$  gas
  - (iii) (C) + MnO<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub>  $\longrightarrow$  Violet vapours
  - (iv) (D) +  $K_2Cr_2O_7$  +  $H_2SO_4$   $\longrightarrow$  Green coloured solution
  - $\begin{array}{ccc}
    (v) & (E) & \xrightarrow{\text{Heat}} & \text{Yellow compound} \\
    \hline
    & \text{Colourless} & \\
    & & \text{solid} & \\
    \end{array}$
- 41. (i) A black coloured compound (B) is formed on passing hydrogen sulphide through the solution of a compound (A) in NH<sub>4</sub>OH.
  - (ii) (B) on treatment with hydrochloric acid and KClO<sub>3</sub> gives (A).
  - (iii) (A) on treatment with potassium cyanide gives a buff coloured precipitate which dissolves in excess of this reagent forming a compound (C).
  - (iv) The compound (C) is changed into a compound (D) when its aqueous solution is boiled.
  - (v) The solution of (A) was treated with excess of sodium bicarbonate and then with bromine water. On cooling and shaking for sometime, a green colour of compound (E) is formed. No change is observed on heating.

Identify (A) to (E) and give chemical equations for the reactions at steps (i) to (v). [Roorkee 1996]

[Hint: The compound (A) is a cobalt salt (CoCl<sub>2</sub>).

(i) 
$$CoCl_2 + 2NH_4OH + H_2S \longrightarrow CoS + 2NH_4Cl + 2H_2O$$
(A) Black
(B)

(ii) CoS + 2HCl + O (from  $KClO_3$ )  $\longrightarrow CoCl_2 + H_2O + S$ 

(iii) 
$$CoCl_2 + 2KCN \longrightarrow Co(CN)_2 + 2KCl$$
Buff coloured
 $Co(CN)_2 + 4KCN \longrightarrow K_4[Co(CN)_6]$ 

- (iv)  $2K_4Fe(CN)_6 + H_2O + O$  (from air)  $\longrightarrow 2K_3Fe(CN)_6 + 2KOH$
- (v)  $CoCl_2 + 6NaHCO_3 \rightarrow Na_4[Co(CO_3)_3] + 2NaCl + 3CO_2 + 3H_2O$  $2Na_4[Co(CO_3)_3] + H_2O + O \longrightarrow 2Na_3[Co(CO_3)_3] + 2NaOH]$
- **42.** A colourless inorganic compound (A) is soluble in water, alcohols and amines. On strong heating (A) gives a brown gas (B) and a grey residue (C). On dissolution of (A) in NH<sub>3</sub>, a solution (D) is formed which reduces aldehydes to form silver mirror. FeSO<sub>4</sub> reduces solution of (A) in water. Aqueous solution of (A) also gives a brick red precipitate (E) with K<sub>2</sub>CrO<sub>4</sub> solution. Identify (A) to (E).
- **43.** A colourless solid (A) on hydrolysis produces a heavy white precipitate (B). Solid (A) gives a clear solution in conc. HCl; however, when added to large amount of water, it again gives precipitate of (B). When H<sub>2</sub>S is passed through a suspension

of (A) or (B), a brown black precipitate of (C) is obtained. Compound (A) liberates a gas (D) on treating with  $H_2SO_4$ . The gas (D) is water soluble and gives white precipitate (E) with solution of mercurous salt but not with mercuric salt. Identify (A) to (E). Also report (A), (B) and (C) if (C) is orange precipitate.

- 44. An inorganic compound (A) in its aqueous solution produced a white ppt. with NaOH, which gets dissolved in excess of NaOH. The aqueous solution of (A) also produced white ppt. with NH<sub>4</sub>OH which also dissolved in excess of NH<sub>4</sub>OH. Also its aqueous solution produced light yellow ppt. with AgNO<sub>3</sub> solution, soluble in dil. HNO<sub>3</sub>. Identify (A).
- 45. When a green solid (A) is fused with sodium carbonate in open air, a coloured salt (B) is formed. A solution of pure (B) gives a coloured precipitate with solutions of lead and barium salts. On extracting (B) with water and adding sulphuric acid, a further colour change takes place and crystals of (C) are obtained on evaporation. When warmed with alcohol, an acidified solution of (C) emits a characteristic smell and on evaporation and cooling, deposits dark violet crystals (D). On warming (C) with ammonium sulphate a colourless gas is produced and (A) is reformed. Identify (A), (B), (C) and (D) and explain the reactions involved.
- 46. There are two metal carbonates (A) and (B), which are insoluble in water but soluble in acetic acid with the evolution of CO<sub>2</sub>. When potassium chromate is added to their solution, (A) gives a yellow precipitate which gives pale green colouration in flame test. The precipitate is filtered out. The filtrate is treated with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, white ppt. is formed which gives crimson red colour in flame test. Identify (A) and (B) and also give equation for the reaction involved.
- 47. A colourless solid (A) on heating gives a white solid (B) and a colourless gas (C). (B) gives a reddish brown gas on treatment with dil. acids. When (B) is heated with solid NH<sub>4</sub>Cl, a colourless gas (D) and a residue (E) are obtained. When (A) is heated with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> a colourless gas (F) is obtained alongwith a white residue (G). Both (E) and (G) imparts yellow colour to flame. The gas (C) reacts with Mg to give white powder. The gas (D) is heated with calcium and the product on hydrolysis gives NH<sub>3</sub>. Identify (A) to (G).
- **48.** A white compound (A) on red heating decomposes to give a residue (B) and two gases (C) and (D). The gas (C) burns with a blue flame. The gas (D) turns lime water milky. The residue (B) on dissolving in water gives heat and solution is alkaline to litmus. The compound (A) imparts brick-red colour to flame. Identify (A) to (D).
- 49. A hydrated metallic salt (A), light green in colour, on careful heating gives a white anhydrous residue (B). (B) is soluble in water and its aqueous solution reacts with NO to give a dark brown compound (C). (B) gives a brown residue (D) and a mixture of two gases (E) and (F). The gases when passed through an acidified KMnO<sub>4</sub> solution discharges the pink colour and when passed through acidified BaCl<sub>2</sub> solution gave a white precipitate. Identify (A), (B), (C), (D), (E) and (F). [M.L.N.R. 1996]
- **50.** A salt is coloured. The anion with barium chloride gives white precipitate insoluble in conc. HNO<sub>3</sub>. When the solution

of this salt is treated with HCl, no precipitate is formed. When H<sub>2</sub>S is passed, no precipitate is formed. When NH<sub>4</sub>Cl and NH<sub>4</sub>OH are added, no precipitate is formed. H<sub>2</sub>S is passed when black precipitate is formed. The precipitate is dissolved in aqua-regia and dimethylglyoxime solution is added in ammonical solution when red precipitate is formed. Find the salt.

- **51.** An aqueous solution of salt gave the following reactions:
  - (i) With barium chloride solution, white precipitate insoluble in HCl is obtained.
  - (ii) Addition of excess KI gives a brown precipitate which turns white on addition of excess of hypo.
  - (iii) With potassium ferrocyanide solution, chocolate coloured precipitate is formed. Identify the salt.
- **52.** (i) The solution of salt (A) in dilute HCl gives a dirty yellow precipitate on passing H<sub>2</sub>S gas. The precipitate dissolves in yellow ammonium sulphide.
  - (ii) The salt (A) gives chromyl chloride test.
  - (iii) (A) first forms a white precipitate with NaOH which dissolves in excess of NaOH forming a compound (B).
  - (iv) The alkaline solution of (B) when added to bismuth chloride gives a black precipitate (C).
  - (v) (A) reduces HgCl<sub>2</sub> in solution to a white precipitate (D) which changes to grey. Identify (A), (B), (C) and (D). Give reactions at steps (i) to (v).

[Hint: The steps (i) and (ii) indicate that (A) is SnCl<sub>2</sub>.

(i) 
$$\begin{array}{ccc} SnCl_2 + H_2S & \longrightarrow & SnS + 2HCl \\ (A) & & Dirty & yellow \\ SnS + (NH_4)_2S_2 & \longrightarrow & SnS_2 + (NH_4)_2S \\ SnS_2 + (NH_4)_2S & \longrightarrow & (NH_4)_2SnS_3 \\ & & Soluble \end{array}$$

(iii) 
$$SnCl_2 + 2NaOH \longrightarrow_{\epsilon} Sn(OH)_2 + 2NaCl$$
  
White ppt.  $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2$  (Sodium stannite)

(B)
Soluble

(iv) 
$$3\text{Na}_2\text{SnO}_2 + 6\text{NaOH} + 2\text{BiCl}_3 \longrightarrow 2\text{Bi} + 3\text{Na}_2\text{SnO}_3$$
(B)
(C)
Black ppt.
+  $6\text{NaCl} + 3\text{H}_2\text{O}$ 

(v) 
$$\operatorname{SnCl}_2 + 2\operatorname{HgCl}_2 \longrightarrow \operatorname{Hg}_2\operatorname{Cl}_2 + \operatorname{SnCl}_4$$

(D)

White ppt.

(Mercurous chloride)

 $\operatorname{Hg}_2\operatorname{Cl}_2 + \operatorname{SnCl}_2 \longrightarrow 2\operatorname{Hg} + \operatorname{SnCl}_4$ 

Grey

**53.** Identify the unknown species and complete the following equations:

(i) 
$$Na_2B_4O_7 \cdot 10H_2O + conc. H_2SO_4 \xrightarrow{\text{Heat}} (A)$$
  
 $\xrightarrow{(B)} (C_2H_5)_3BO_3$   
(ii)  $Na_3PO_4 + (NH_4)_2MoO_4 + HNO_3 \longrightarrow (C)$ 

Yellow ppt.

(iii) 
$$\text{NaF} + \text{H}_2 \text{SO}_4 + \text{SiO}_2 \longrightarrow (D)$$
 
$$(D) + \text{H}_2 \text{O} \longrightarrow (E)$$
 White (Silicic acid)

(iv) 
$$K_2Cr_2O_7 + KCl + conc. H_2SO_4 \longrightarrow Reddish$$
  
brown vapours (F)

$$(F)$$
 + NaOH  $\longrightarrow$  Yellow solution  $(G)$ 

$$(G) + (CH_3COO)_2 Pb \longrightarrow Yellow ppt. (H)$$

#### **54.** Identify the gas (X):

- (i) (X) is a colourless with pungent smell.
- (ii) (X) turns lime water milky.
- (iii) (X) turns acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution green.
- (iv) (X) decolourises acidified KMnO<sub>4</sub> solution.
- (v) (X) gives white turbidity when  $H_2S$  is passed through it aqueous solution.
- (vi) A white precipitate insoluble in conc. HNO<sub>3</sub> is formed when the aqueous solution of (X) in NaOH is treated with barium chloride and bromine water.

[Hint: (i) (X) is SO<sub>2</sub>. It is colourless and pungent. Rest of properties are observed with SO<sub>2</sub>.

(ii) 
$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O$$
Lime water Milky

(iii) 
$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O_{Green}$$

(iv) 
$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
  
 $[SO_2 + O + H_2O \longrightarrow H_2SO_4] \times 5$ 

(vi) 
$$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$$
  
 $Na_2SO_3 + BaCl_2 \longrightarrow BaSO_3 + 2NaCl$   
 $Br_2 + H_2O \longrightarrow 2HBr + [O]$   
 $BaSO_3 + [O] \longrightarrow BaSO_4$   
White ppt.

(Insoluble in conc. HNO<sub>3</sub>)]

55. (A)  $\xrightarrow{\text{KOH}, \text{H}_2\text{O}_2}$  (B)  $\xrightarrow{\text{Cl}_2}$  (C)

Black substance Green Pink-violet

HCl HCl

Pale green gas  $\xrightarrow{\text{KI}}$  Violet vapours of iodine

(C) is a volumetric reagent. It can be used for estimation of ferrous sulphate and oxalic acid in acidic medium without employing any indicator.

Identify (A), (B), (C) and (D). Give all reactions.

56. A colourless salt (A) gives a mixture of three gases (B), (C) and (D) along with water vapours. Gas (B) is basic, (C) is acidic while (D) is neutral in nature. Gas (B) is also evolved when (A) is heated with KOH and gives brown precipitate with Nessler's reagent. The gas (C) when passes through lime water, gives white turbidity. Magnesium burns in the atmosphere of gas (C). The gas (D) burns with blue flame and is formed when potassium ferrocyanide is heated with

conc.  $H_2SO_4$ . The solution of (A) in water forms a white precipitate (E) with calcium chloride solution. The precipitate (E) decolourises acidified KMnO<sub>4</sub> solution.

Identify (A) to (E) and explain reactions.

- 57. (i) A black coloured compound (B) is formed on passing hydrogen sulphide through the solution of (A) in NH<sub>4</sub>OH.
  - (ii) (B) on treatment with aqua-regia gives (A).
  - (iii) The solution of (A) is treated with excess of sodium bicarbonate and then with NaOH and bromine water. No apple green colour is observed. The solution is heated, when a black precipitate (C) is obtained.
  - (iv) (A) on treatment with potassium cyanide gives a buff coloured precipitate which dissolves in excess of this reagent forming a compound (D).

Identify (A) to (D) and give chemical equations for the reactions at steps (i) to (iv).

- **58.** Explain with proper reasoning:
  - (i) The aqueous solution of ferric chloride cannot be stored. It is always acidified with hydrochloric acid.

[Hint: Ferric chloride is a salt of weak base and a strong acid. Its hydrolysis occurs readily with the formation of Fe(OH)<sub>3</sub> ppt.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$
  
The addition of HCl prevents hydrolysis.]

(ii) The aqueous solution of FeCl<sub>3</sub> possesses yellow colour, but the colour becomes green on passing H<sub>2</sub>S gas.

[Hint: Reduction of FeCl<sub>3</sub> occurs into ferrous chloride which gives green coloured solution.

$$\begin{array}{ccc} 2\text{FeCl}_3 + \text{H}_2\text{S} & \longrightarrow & 2\text{FeCl}_2 + 2\text{HCl} + \text{S}] \\ \text{Yellow} & & \text{Green} \end{array}$$

(iii) The aqueous solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is orange. On adding an alkali, it turns yellow.

[Hint: In presence of alkali, dichromate changes to chromate.

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$
Orange Yellow

(iv) In the test of oxalate, the evolved gas burns with blue flame only initially.

[Hint: CO is evolved along with CO<sub>2</sub>.CO burns with blue flame while CO<sub>2</sub> prevents its burning.

$$H_2C_2O_4 \xrightarrow{\text{Heat}} H_2O + CO + CO_2$$

CO diffuses faster than CO<sub>2</sub>. Once CO burns with blue flame, it is put off by CO<sub>2</sub> which diffuses later.]

(v) Why yellow ammonium sulphide is used in group (II) sulphides separation?

[Hint: Yellow ammonium sulphide possesses excess of free sulphur. It combines with stannous sulphide (SnS) to convert it to stannic sulphide (SnS<sub>2</sub>) which forms soluble complex with (NH<sub>4</sub>)<sub>2</sub>S.

$$SnS + S \longrightarrow SnS_2$$

$$SnS_2 + (NH_4)_2S \longrightarrow (NH_4)_2SnS_3$$

**Note:** In case, tin compound is not present in the mixture, ordinary ammonium sulphide can be used instead of yellow ammonium sulphide.

(vi) Why zinc sulphide is not precipitated when H<sub>2</sub>S is passed through ZnCl<sub>2</sub> solution?

[Hint: The reaction of ZnCl<sub>2</sub> and H<sub>2</sub>S produces HCl which dissolves ZnS.

$$ZnCl_2 + H_2S \longrightarrow ZnS + 2HCl$$

(vii) CaSO<sub>4</sub> is insoluble but is not precipitated when excess of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is added to CaCl<sub>2</sub>.

[Hint : The precipitate of  $CaSO_4$  dissolves in  $(NH_4)_2SO_4$  forming a complex (double sulphate).

 $CaSO_4 + (NH_4)_2SO_4 \longrightarrow (NH_4)_2Ca(SO_4)_2$ Soluble

(viii) Why (NH<sub>4</sub>Cl+NH<sub>4</sub>OH) and not [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>+NH<sub>4</sub>OH] is used in group (III) analysis?

[Hint: The presence of sulphate ions brings precipitation of various basic ions such as Ca<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, etc.]

(ix) Why is it necessary to add few drops of conc. HNO<sub>3</sub> to the filtrate of group (II) before the use of NH<sub>4</sub>Cl + NH<sub>4</sub>OH?

[Hint: The addition of few drops of conc. HNO<sub>3</sub> serves two purposes.

- (a) It precipitates the dissolved H<sub>2</sub>S.
- (b) It converts ferrous ion into ferric ion if iron is present.]
- (x) Why NaOH cannot be used to separate Al(OH)<sub>3</sub> and Zn(OH)<sub>2</sub>?

[Hint: Both the hydroxides dissolve in NaOH.

Al(OH)<sub>3</sub> + NaOH → NaAlO<sub>2</sub> + 2H<sub>2</sub>O Soluble

 $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$ Soluble

### Answers

#### **Answers:** Subjective Type Questions

- 18. PbCl<sub>2</sub>; AgCl; Hg<sub>2</sub>Cl<sub>2</sub>, PbCl<sub>2</sub> is soluble in hot water.
- 21. PbSO<sub>4</sub> is soluble in ammonium acetate (3%).

PbSO<sub>4</sub> + 2CH<sub>3</sub>COONH<sub>4</sub>  $\longrightarrow$  Pb(CH<sub>3</sub>COO)<sub>2</sub> + (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> AgCl is soluble in ammonium hydroxide.

 $AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O$ 

BaSO<sub>4</sub> is boiled with concentrated solution of sodium carbonate. The barium carbonate is then dissolved in dil. acetic acid.

 $BaSO_4 + Na_2CO_3 \longrightarrow BaCO_3 + Na_2SO_4$ 

 $BaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ba + CO_2 + H_2O$ HgS is dissolved in aqua-regia.

 $3HgS + 2HNO_3 + 6HCl \longrightarrow 3HgCl_2 + 2NO + 3S + 4H_2O$ 

22. (a) Lead salt + sodium sulphide.

 $Pb(CH_3COO)_2 + Na_2S \longrightarrow PbS + 2CH_3COONa$ Black

 $\label{eq:HgCl2} \text{HgCl}_2 + 2\text{KI} \xrightarrow{} \text{HgI}_2 + 2\text{KCl} \\ \text{Red}$ 

 $HgI_2 + 2KI \longrightarrow K_2HgI_4$ Soluble

(c)  $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$  White ppt.

 $\begin{array}{c} AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O \\ Soluble \end{array}$ 

 $\begin{array}{ccc} \text{(d)} & & Pb(\text{NO}_3)_2 \, + \, 2KI \longrightarrow PbI_2 \, + \, 2KNO_3 \\ & & \text{Yeliow ppt.} \end{array}$ 

- 28. CdS and As<sub>2</sub>S<sub>3</sub>.
- 29. (a)  $CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2 + (NH_4)_2SO_4$

 $Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \longrightarrow Cu(NH_3)_4SO_4 + 4H_2O$ (b)  $2BiCl_3 + 3Na_2SnO_2 + 6NaOH \longrightarrow 2Bi + 3Na_2SnO_3 + 6NaCl$ 

+ 3H<sub>2</sub>O

- (c)  $2\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$  $\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \longrightarrow 2\text{Hg} + \text{SnCl}_4$
- (d)  $SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$
- 31. (c) Al(OH)<sub>3</sub> dissolves in NaOH.

  Al(OH)<sub>3</sub> + NaOH  $\longrightarrow$  NaAlO<sub>2</sub> + 2H<sub>2</sub>O

- 40. (i) sulphate, (ii) ammonium salt, (iii) iodide (iv) reducing agent such as sulphite, SO<sub>2</sub>, sulphide, H<sub>2</sub>S, nitrite, etc., (v) ZnO.
- **42.** (A) AgNO<sub>3</sub>; (B) NO<sub>2</sub>; (C) Ag; (D)  $[Ag(NH_3)_2]^+$ ; (E) Ag<sub>2</sub>CrO<sub>4</sub>
- 43. (A) BiCl<sub>3</sub>; (B) BiOCl; (C) Bi<sub>2</sub>S<sub>3</sub>; (D) HCl; (E) Hg<sub>2</sub>Cl<sub>2</sub>
- 44. AlBr<sub>3</sub>
- **45.** (A) Cr<sub>2</sub>O<sub>3</sub>; (B) Na<sub>2</sub>CrO<sub>4</sub>; (C) Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>; (D) NaCr(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O
- **46.** BaCO<sub>3</sub>, SrCO<sub>3</sub>
- **47.** (A) NaNO<sub>3</sub>; (B) NaNO<sub>2</sub>; (C) O<sub>2</sub>; (D) N<sub>2</sub>; (E) NaCl; (F) N<sub>2</sub>O; (G) Na<sub>2</sub>SO<sub>4</sub>
- **48.** (A)  $CaC_2O_4$ ; (B) CaO; (C) CO; (D)  $CO_2$
- **49.** (A) FeSO<sub>4</sub>·7H<sub>2</sub>O; (B) FeSO<sub>4</sub>; (C) FeSO<sub>4</sub>NO; (D) Fe<sub>2</sub>O<sub>3</sub>; (E) SO<sub>2</sub>; (F) SO<sub>3</sub>
- **50.** NiSO<sub>4</sub>
- 51. CuSO<sub>4</sub>
- **53.** (i)  $Na_2B_4O_7 \cdot 10H_2O + H_2SO_4 \longrightarrow Na_2SO_4 + 4H_3BO_3 + 5H_2O$  (A)  $H_3BO_3 + 3C_2H_5OH \longrightarrow (C_2H_5)_3BO_3 + 3H_2O$

(A) (B)
Boric acid Ethyl alcohol

(ii)  $Na_3PO_4+12(NH_4)_2MoO_4+24HNO_3 \rightarrow (NH_4)_3PO_4\cdot12MoO_3$ Yeliow ppt. (C)

+ 21NH<sub>4</sub>NO<sub>3</sub> + 3NaNO<sub>3</sub> + 12H<sub>2</sub>O

- (iii)  $4\text{NaF} + 2\text{H}_2\text{SO}_4 + \text{SiO}_2 \longrightarrow \text{SiF}_4 + 2\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$   $3\text{SiF}_4 + 4\text{H}_2\text{O} \longrightarrow 2\text{H}_2\text{SiF}_6 + \text{H}_4\text{SiO}_4$ (D) (E)
- (iv)  $K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + 3K_2SO_4 + 3H_2O_4$

 $\operatorname{CrO_2Cl_2} + 4\operatorname{NaOH} \longrightarrow \operatorname{Na_2CrO_4} + 2\operatorname{NaCl} + 2\operatorname{H_2O}$  (F)

- $Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4 + 2CH_3COONa$ (G)
  (H)
- 55. (A)  $MnO_2$ ; (B)  $K_2MnO_4$ ; (C)  $KMnO_4$ ; (D)  $Cl_2$
- **56.** (A)  $(NH_4)_2C_2O_4$ ; (B)  $NH_3$ ; (C)  $CO_2$ ; (D)  $CO_3$ ; (E)  $CaC_2O_4$
- 57. (A) NiCl<sub>2</sub>; (B) NiS; (C) Ni<sub>2</sub>O<sub>3</sub>; (D) K<sub>2</sub>Ni(CN)<sub>4</sub>

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS



- 1. A salt made of bivalent ions X and Y, each of which is capable of decolourising acidified KMnO<sub>4</sub> solution. The salt is likely
  - (a) stannic chloride
- (b) ferric sulphate
- (c) ferrous sulphate
- (d) ferrous oxalate

Ans. (d)

[Hint: Ferrous oxalate consists of Fe<sup>2+</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions. Both act as reducing agents and decolourise acidified KMnO4

$$2MnO_4^- + 16H^+ + 10Fe^{2+} \longrightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O$$
  
 $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + \cdot 10CO_2 + 8H_2O]$ 

- 2. Which of the following salt will evolve sulphur dioxide gas along with formation of yellowish turbidity when treated with dilute H2SO4?
  - (a) Sodium sulphide
- (b) Sodium sulphite
- (c) Sodium thiosulphate
- (d) Sodium sulphate

Ans. (c)

[Hint: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is decomposed by dilute H<sub>2</sub>SO<sub>4</sub> giving free sulphur and evolving SO<sub>2</sub> gas.

$$Na_2S_2O_3 + H_2SO_4 \longrightarrow Na_2SO_4 + S + SO_2 + H_2O]$$
(Yellowish turbidity)

- 3. A colourless salt gives white precipitate with CaCl<sub>2</sub> solution. The salt also decolourises acidified MnO<sub>4</sub> with effervescence. On reaction with conc. H<sub>2</sub>SO<sub>4</sub>, the salt gives a colourless gaseous mixture containing:
  - (a)  $CO, CO_2$
- (b)  $CO_2$ ,  $SO_2$
- (c) CO<sub>2</sub>, H<sub>2</sub>S
- (d)  $CO, SO_2$

Ans. (a)

[Hint: The colourless salt is an oxalate which on reaction with conc. H<sub>2</sub>SO<sub>4</sub> gives a gaseous mixture CO and CO<sub>2</sub>. The salt gives a white ppt. with CaCl2 solution and decolourises acidified KMnO<sub>4</sub> solution.

$$C_{2}O_{4}^{2-} + Ca^{2+} \longrightarrow CaC_{2}O_{4};$$

$$5C_{2}O_{4}^{2-} + 16H^{+} + 2MnO_{4}^{-} \longrightarrow 2Mn^{2+} + 10CO_{2} + 8H_{2}O;$$

$$C_{2}O_{4}^{2-} + 2H^{+} \longrightarrow CO + CO_{2} + H_{2}O]$$

- Aqueous solution of a salt + MgSO<sub>4</sub> solution  $\longrightarrow$  no ppt. Heating a white ppt. appears. The salt contains the acidic radical:
  - (a)  $CO_3^{2-}$

(c)  $SO_3^2$ 

(d)  $C_2O_4^2$ 

[Hint: Bicarbonate ion does not give ppt. with MgSO<sub>4</sub> in cold but on heating, a white ppt. appears.

$$Mg^{2+} + 2HCO_3^- \longrightarrow Mg(HCO_3)_2 \xrightarrow{Heat} MgCO_3 + CO_2 + H_2O$$
 ]

Soluble White ppt.

5. Which of the following is formed when CO<sub>2</sub> gas is passed through an aqueous solution of sodium chromate?

- (a) Cr(OH)<sub>3</sub> is precipitated
- (b) Yellow solution of Cr<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> is formed
- (c) Orange solution of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is formed
- (d) No reaction

Ans. (c)

[Hint: CO2 makes the solution acidic. Under acidic conditions, Na<sub>2</sub>CrO<sub>4</sub> is converted into Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.1

In the reactions,

$$K_2Cr_2O_7 + KCl + Conc. H_2SO_4 \xrightarrow{\text{Heat}} A \xrightarrow{\text{NaOH}} B.$$
 A is reddish brown gas soluble in NaOH forming B. A and B are:

- (a) CrO<sub>2</sub>Cl<sub>2</sub>, Na<sub>2</sub>CrO<sub>4</sub>
- (b) CrO<sub>2</sub>Cl<sub>2</sub>, Na<sub>2</sub>Cr<sub>2</sub>O<sub>4</sub>
- (c) CrO<sub>2</sub>Cl<sub>2</sub>, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
- (d) CrO<sub>2</sub>Cl, Na<sub>2</sub>CrO<sub>4</sub>

Ans. (a)

Ans. (a)
$$[\textbf{Hint}: K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow \\ 6KHSO_4 + 2CrO_2Cl_2 + 3H_2O \\ \text{Reddish} \\ \text{brown gas} \\ (A)$$

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O ] \longrightarrow \\ CrO_2Cl_2 + 4NaOH \longrightarrow \\ CrO_2Cl$$

- 7. As<sub>2</sub>S<sub>3</sub> dissolves in a solution of yellow ammonium sulphide to give:
  - (a)  $(NH_4)_2AsO_2$
- (b)  $(NH_4)_3AsS_3$
- (c)  $(NH_4)_3AsS_4$
- (d)  $(NH_4)_3AsS_5$

Ans. (c)

- [Hint:  $As_2S_3 + 2(NH_4)_2S_2 \longrightarrow As_2S_5 + 2(NH_4)_2S$  $As_2S_5 + 3(NH_4)_2S \longrightarrow 2(NH_4)_3AsS_4$
- 8. Which of the following sulphide is completely precipitated only when the acidic solution is made dilute?
  - (a) HgS

(b) PbS

(c) CuS

- (d) CdS
- Ans. (d)
- Which of the following compound on reaction with NaOH and Na<sub>2</sub>O<sub>2</sub> gives yellow colour?
  - (a) Cr(OH)<sub>3</sub>
- (b)  $Zn(OH)_2$
- (c) Al(OH)<sub>3</sub>
- (d) None of these

Ans. (a) [Hint:  $2Cr(OH)_3 + 3[O] + 4NaOH \longrightarrow 2Na_2CrO_4 + 5H_2O$ ] (From Na2O2)

- 10. In group V,  $(NH_4)_2CO_3$  is added to precipitate out carbonates. In place of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, why Na<sub>2</sub>CO<sub>3</sub> cannot be used because:
  - (a) CaCO<sub>3</sub> is soluble in Na<sub>2</sub>CO<sub>3</sub>
  - (b) MgCO<sub>3</sub> will be precipitated
  - (c) Double carbonates are precipitated
  - (d) None of the above

Ans. (b)

### **OBJECTIVE QUESTIONS**



**Note:** Choose the correct answer out of given alternatives for each question.

I.	Which of the following gives a suffocating gas when treated	11.	Aqueous solution of A gives yellow precipitate with aque	
	with dilute HCl?	1	solution of K <sub>2</sub> CrO <sub>4</sub> . Which of the following series of cat	ions
	(a) carbonate $\Box$ (b) sulphite $\Box$	1	may be present in 'A':	
_	(c) sulphate $\Box$ (d) borate $\Box$		(a) $Pb^{2+}$ , $Ag^{+}$	
2.	The acidic solution of a salt produces blue colour with KI		(c) $Ag^+$ , $Cu^{2+}$	
	starch solution. The salt may be:	12.	Mercurous chloride turns black on treatment with ammon	iium
	(a) sulphite $\Box$ (b) bromide $\Box$		hydroxide. This is due to the formation of:	
	(c) nitrite $\Box$ (d) chloride $\Box$	l	(a) $Hg(NH_2)Cl$	
3.	Sulphite on treatment with dil. H <sub>2</sub> SO <sub>4</sub> liberates a gas which:		(c) Hg and HgNH <sub>2</sub> Cl $\Box$ (d) HgCl <sub>2</sub> ·NH <sub>4</sub> OH	
	(a) turns lead acetate paper black	13.	A light yellow precipitate is formed in the second grou	p of
-	(b) burns with blue flame		the qualitative analysis on passing H <sub>2</sub> S even when no rac	
	(c) smells like vinegar		of second group is present. This is due to the presence	
	(d) turns acidified $K_2Cr_2O_7$ paper green	1	in the mixture.	
4.	In the ring test for nitrates, the ring formed is due to:		(a) phosphate	
	(a) $FeSO_4 \cdot NO$ $\square$ (b) $FeSO_4 \cdot NO_2$ $\square$		(c) oxalate	
	(c) $Fe(NO_3)_3$ $\square$ (d) $Fe_2(SO_4)_3 \cdot NO$ $\square$	14.	An orange precipitate in the second group is given by	:
5.	Violet vapours are given out whenis treated with		(a) $Sb^{3+}$	
	conc. H <sub>2</sub> SO <sub>4</sub> .	)	(c) $Hg^{2+}$ $\Box$ (d) $As^{3+}$	<u> </u>
	(a) bromide $\Box$ (b) iodide $\Box$	15	A precipitate of which of the following would be obta	_
	(c) chloride $\Box$ (d) nitrate $\Box$	15.	when HCl is added to a solution of stannous sulphide (\$\frac{1}{2}\$)	
6.	Oxalate + MnO <sub>2</sub> + dil. $H_2SO_4 \longrightarrow Gas$ . The gas evolved is:	[	in yellow ammonium sulphide?	)IIO)
	(a) $CO_2$	ſ	*	П
	(c) $SO_2$ $\square$ (d) $O_2$ $\square$	,	(a) $SnS$ $\square$ (b) $SnS_2$	
7.	When a mixture containing phosphate is heated with conc.		(c) $(NH_4)_2SnS_2$ $\square$ (d) $Sn_2S_3$	
	HNO <sub>3</sub> and ammonium molybdate solution, a canary yellow	16.	On heating a mixture of NaCl, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> and conc. H <sub>2</sub>	$_2SO_4$
	precipitate is formed. The formula of the yellow precipitate	1	which of the following is formed?	
	is:	ĺ	(a) $CrCl_3$	
	(a) $(NH_4)_3PO_4$	]	(c) $Cl_2$ $\Box$ (d) $NaClO_2$	
	(b) $(NH_4)_3PO_4$ ·12MoO <sub>4</sub>	17.		ound
	(c) $(NH_4)_3PO_4$ · $12MoO_3$	}	formed is:	_
	(d) $(NH_4)_3 \cdot PO_4 \cdot (NH_4)_2 \cdot MoO_4$	1	(a) $Bi_2O_3$	
8.	Conc. H <sub>2</sub> SO <sub>4</sub> is put into two test tubes 'A' containing a	1	(c) $BiOCl$ $\Box$ (d) $BiOCl_2$	
	nitrate salt and 'B' containing a bromide salt and the contents	18.	Ferric ion forms a prussian blue coloured precipitate	with
	are heated to evolve reddish brown gases which were passed	ĺ	$K_4[Fe(CN)_6]$ due to the formation of:	
	through water. Water will:	}	(a) $K_3Fe(CN)_6$ $\square$ (b) $Fe_4[Fe(CN)_6]_3$	
	(a) turn yellow by gas coming from test tube 'A'	1	(c) $Fe(OH)_3$	
	(b) turn brown by gas coming from test tube 'A' □	19.	The sulphide which is insoluble in 30% HNO <sub>3</sub> is:	
	(c) turn blood red by gas coming from test tube 'B'		(a) HgS	
	(d) turn yellow by gas coming from test tube 'B'		(c) PbS	
	[Hint: Bromine gas coming from test tube 'B' turns the water	20.	The basic radical which is tested by the reagent and	
_	brownish yellow.]	20.	used for the test of phosphate is:	aiso
9.	The colour developed, when sodium sulphide is added to	1	(a) $Cd^{2+}$ $\Box$ (b) $Sn^{2+}$	
	sodium nitroprusside is:	1	(a) Cu	
	(a) violet	21	(c) $Sb^{3+}$ $\Box$ (d) $As^{3+}$	
10	(c) red	21.	NiS is separated from ZnS by treating with:	
10.	A gas is evolved which burns with blue flame when the	Ì	(a) NaOH	님
	mixture is heated with conc. H <sub>2</sub> SO <sub>4</sub> . The mixture contains:		(b) conc. HCl	
	(a) carbonate	1	(c) yellow ammonium sulphide	
	(c) nitrate $\Box$ (d) nitrite $\Box$	1	(d) aqua-regia	

					1
Qua	litative Inorganic Analysis			911	
22.	Manganese salt + PbO <sub>2</sub> + conc. HNO <sub>3</sub> → The solution	n 1		(c) a red coloured ppt. is obtained	1
	acquires purple colour. The colour is due to:	*		(d) a black coloured ppt. is obtained	
	(a) HMnO <sub>4</sub>	1   ·	34	All ammonium salts liberate ammonia when:	•
	(c) $Mn(NO_3)_2$ $\square$ (d) $H_2MnO_4$ $\square$	- 1	J 1.	(a) heated	1
23.		- 1		(b) heated with caustic soda	
	yellow precipitate is:			(c) heated with H <sub>2</sub> SO <sub>4</sub>	
	(a) potassium cobaltonitrite	1		(d) heated with NaNO <sub>2</sub>	
	(b) potassium cobaltinitrite	1	35.	2	-
	(c) cobalt nitrite	1		(a) CaCO <sub>3</sub>	1
	(d) cobalt nitrate	_ 1		(c) $Sr(NO_3)_2$ $\square$ (d) $BaCl_2$ $\square$	
24.		_ [	36.	(-)	
~	(a) $(NH_4)_2CO_3$ $\square$ (b) $(NH_4)_2SO_4$ $\square$	. }	50,	NaOH?	•
	(c) NH <sub>4</sub> Cl $\Box$ (d) (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> $\Box$			(a) $Fe(OH)_3$ $\Box$ (b) $Al(OH)_3$	]
25.	Dimethyl glyoxime is used for the test ofi	- 1		(c) $Cr(OH)_3$ $\Box$ (d) $Mn(OH)_2$	
٠.	alkaline medium:		37.	1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1	
	(a) cobalt	l l	•	concentrated H <sub>2</sub> SO <sub>4</sub> . No action is observed in either case	
	(c) manganese			The solid contains:	
-26-	Sulphuric acid is not used for the preparation of original			(a) sulphide	]
	solution in the analysis of basic radicals because:	.		(c) sulphate	
	(a) it is a strong oxidising agent	٦	38.	, , , , , , , , , , , , , , , , , , ,	
	(b) it is a strong reducing agent	- 1		gas because:	
	(c) it forms insoluble sulphates with some of the basis			(a) the sulphides of IV group are insoluble in NH <sub>4</sub> OH	]
		j  -		(b) the sulphides of other metals are soluble in NH <sub>4</sub> OH	]
	(d) it decomposes many of the anions			(c) the concentration of $S^{2-}$ ions is high enough to	0
27.		-		precipitate the sulphides of IV group	
		a		(d) the sulphides of second group are soluble in NH <sub>4</sub> OHE	]
			39.		
28.	**	_		(a) acetic acid	J .
	turns lead acetate paper black. It is:	_		(c) HNO <sub>3</sub>	]
	2 7	a	40.	Ethyl borate burns with:	
	the state of the s	<u> </u>		(a) yellow flame	J
29.	A mixture when rubbed with organic acid smells like vinega	r.		(c) blue flame	]
	It contains:		41.	Which one of the following pairs of ions cannot be separate	d
		ן כ		by H <sub>2</sub> S in dilute HCl?	
		]		(a) $Bi^{3+}$ , $Sn^{4+}$	_
30.	Soda extract is prepared by:			2. 2.	_
	(a) fusing soda and mixture and then extracting with water	r	42.		
		ן כ	<b>4</b> Z.	which of the following cations give precipitate on reaction with KI?	11
	(b) dissolving NaHCO <sub>3</sub> and mixture in dil. HCl	<b>]</b>			_
		<b>」</b>		( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( )	]
		ן כ		(,,, ,,, ,,, ,,, ,,, ,,, ,,, ,,	
31.		of	43.	The brown ring test is performed for the qualitative detection	n
	elements are soluble in yellow ammonium sulphide:			of:	
		ן כ		(-)	_
		ן כ			<u>ק</u>
32.	Warner 1	g	44.	b	
	HCl to a solution of Sb <sub>2</sub> S <sub>3</sub> in yellow ammonium sulphide				_
		<b>]</b>		` '	
		コ	45.		
	[ <b>Hint</b> : $2(NH_4)_3SbS_4 + 6HCl \longrightarrow Sb_2S_5 + 6NH_4Cl + 3H_2S$ ]			(a) HgS	_

(c) CuS

obtained are:

33. When dimethyl glyoxime solution is added to an aqueous

hydroxide:

(a) no precipitate is obtained

(b) a blue coloured ppt. is obtained

solution of nickel (II) chloride followed by ammonium

☐ (d) CdS

46. An aqueous solution of  $FeSO_4 \cdot Al_2(SO_4)_3$  and chrome alum

(a) a colourless filtrate and a green residue

is heated with excess of Na<sub>2</sub>O<sub>2</sub> and filtered. The materials

		1	
	(b) a yellow filtrate and a green residue $\Box$		(a) $CuS > ZnS > Na_2S \square$ (b) $ZnS > Na_2S > CuS \square$
	(c) a yellow filtrate and a brown residue		(c) $Na_2S > CuS > ZnS \square$ (d) $Na_2S > ZnS > CuS \square$
	(d) a green filtrate and a brown residue	58.	When H <sub>2</sub> S gas is passed through the HCl containing
47.	The salt used for performing 'bead test' in qualitative		aqueous solution of CuCl <sub>2</sub> , HgCl <sub>2</sub> , BiCl <sub>3</sub> and CoCl <sub>2</sub> , it does
	inorganic analysis is:		not precipitate out: [P.M.T. (M.P.) 2002]
	(a) $K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$	Ì	(a) CuS
			(c) $Bi_2S_3$ $\Box$ (d) $CoS$ $\Box$
	(b) $FeSO_4$ · $(NH_4)_2SO_4$ · $6H_2O$	59.	In borax bead test which compound is formed?
	(c) $Na(NH_4)HPO_4\cdot 4H_2O$	39.	-
	(d) $CaSO_4 \cdot 2H_2O$		[C.B.S.E., P.M.T. 2002]
48.	The only cations present in a slightly acidic solution are		(a) Orthoborate
,	Fe <sup>3+</sup> , Zn <sup>2+</sup> and Cu <sup>2+</sup> . The reagent which when added in		(c) Double oxide
	excess to this solution would identify and separate Fe <sup>3+</sup> in	60.	Mark the correct statement: [P.M.T. (M.P.) 2002]
	one step is:	{	(a) I group basic radicals precipitate as chlorides
	(a) $2M$ HCl $\Box$ (b) $6M$ NH <sub>3</sub> $\Box$	ļ	(b) IV group basic radicals precipitate as sulphides
	(c) $6 M$ NaOH $\Box$ (d) $H_2S$ gas $\Box$		(c) V group basic radicals precipitate as carbonates
49.	- (2/		(d) All the above statements are correct
49.	mixture of :	61	Potassium chromate solution is added to an aqueous solution
		}	of a metal chloride. The precipitate thus obtained are
	(a) $Al^{3+}$ and $Sn^{2+}$ $\square$ (b) $Al^{3+}$ and $Fe^{3+}$ $\square$		insoluble in acetic acid. These are subjected to flame test
	(c) $Al^{3+}$ and $Zn^{2+}$ $\Box$ (d) $Zn^{2+}$ and $Pb^{2+}$ $\Box$	1	the colour of the flame is: [P.M.T. (Manipal) 2002]
50.	Which one is not the interfering radical?		(a) lilac
	(a) $PO_4^{3-}$ $\square$ (b) $BO_3^{3-}$ $\square$		(c) crimson red $\Box$ (d) golden yellow $\Box$
	(c) $F^ \Box$ (d) $SO_4^{2-}$ $\Box$	62.	Consider the following observation:
51.	The metal ion which is precipitated when $H_2S$ is passed with		$M^{n+}$ + HCl $\longrightarrow$ white precipitate $\stackrel{\triangle}{\longrightarrow}$ water soluble. The
01.	HCl: [C.P.M.T. 2001]		metal ion $M^{n+}$ will be : [D.P.M.T. 2002]
	(a) $\operatorname{Zn}^{2+}$ $\square$ (b) $\operatorname{Ni}^{2+}$ $\square$		(a) $Hg^{2+}$ $\Box$ (b) $Ag^{+}$ $\Box$
	(c) $Cd^{2+}$ $\Box$ (d) $Mn^{2+}$ $\Box$	(	
52.	Which of the following metal sulphides has maximum		
32.		63.	When $H_2S$ is passed through $Hg_2^{2+}$ , we get:
52.	solubility in water? [A.I.I.M.S. 2001]	63.	[A.I.E.E.E. 2002]
32.	solubility in water? [A.I.I.M.S. 2001] (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$	63.	[A.I.E.E.E. 2002] (a) HgS $\square$ (b) HgS + Hg <sub>2</sub> S $\square$
	solubility in water? [A.I.I.M.S. 2001] (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$	63.	[A.I.E.E. 2002] (a) HgS $\square$ (b) HgS + Hg <sub>2</sub> S $\square$ (c) HgS + Hg $\square$ (d) Hg <sub>2</sub> S $\square$
53.	solubility in water? [A.I.I.M.S. 2001] (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes	63.	[A.I.E.E. 2002] (a) HgS (b) HgS + Hg <sub>2</sub> S (c) HgS + Hg (d) Hg <sub>2</sub> S (d) Hg <sub>2</sub> S
	solubility in water? [A.I.I.M.S. 2001] (a) HgS $K_{\rm sp} = 10^{-54}$ $\Box$ (b) CdS $K_{\rm sp} = 10^{-30}$ $\Box$ (c) FeS $K_{\rm sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{\rm sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001]		[A.I.E.E. 2002] (a) HgS $\square$ (b) HgS + Hg <sub>2</sub> S $\square$ (c) HgS + Hg $\square$ (d) Hg <sub>2</sub> S $\square$
	solubility in water? [A.I.I.M.S. 2001]  (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001] (a) Deliquescence $\Box$ (b) Efflorescence $\Box$		[A.I.E.E. 2002] (a) HgS $\Box$ (b) HgS + Hg <sub>2</sub> S $\Box$ (c) HgS + Hg $\Box$ (d) Hg <sub>2</sub> S $\Box$ How do we differentiate between Fe <sup>3+</sup> and Cr <sup>3+</sup> in group III?
53.	solubility in water? [A.I.I.M.S. 2001]  (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001]  (a) Deliquescence $\Box$ (b) Efflorescence $\Box$ (c) Allotropy $\Box$ (d) Sublimation $\Box$		[A.I.E.E. 2002] (a) HgS $\Box$ (b) HgS + Hg <sub>2</sub> S $\Box$ (c) HgS + Hg $\Box$ (d) Hg <sub>2</sub> S $\Box$ How do we differentiate between Fe <sup>3+</sup> and Cr <sup>3+</sup> in group III?  [A.I.E.E. 2002]
53.	solubility in water? [A.I.I.M.S. 2001]  (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001]  (a) Deliquescence $\Box$ (b) Efflorescence $\Box$ (c) Allotropy $\Box$ (d) Sublimation $\Box$ The compound formed in the borax bead test of Cu <sup>2+</sup> ion in		[A.I.E.E. 2002]  (a) HgS  (b) HgS + Hg <sub>2</sub> S  (c) HgS + Hg  (d) Hg <sub>2</sub> S  How do we differentiate between Fe <sup>3+</sup> and Cr <sup>3+</sup> in group III?  [A.I.E.E. 2002]  (a) By adding excess of NH <sub>4</sub> OH solution
53.	solubility in water? [A.I.I.M.S. 2001]  (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001]  (a) Deliquescence $\Box$ (b) Efflorescence $\Box$ (c) Allotropy $\Box$ (d) Sublimation $\Box$		[A.I.E.E. 2002]  (a) HgS $\Box$ (b) HgS + Hg <sub>2</sub> S $\Box$ (c) HgS + Hg $\Box$ (d) Hg <sub>2</sub> S $\Box$ How do we differentiate between Fe <sup>3+</sup> and Cr <sup>3+</sup> in group III?  [A.I.E.E. 2002]  (a) By adding excess of NH <sub>4</sub> OH solution (b) By increasing NH <sup>4</sup> <sub>4</sub> ion concentration $\Box$
53.	solubility in water? [A.I.I.M.S. 2001]  (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001]  (a) Deliquescence $\Box$ (b) Efflorescence $\Box$ (c) Allotropy $\Box$ (d) Sublimation $\Box$ The compound formed in the borax bead test of Cu <sup>2+</sup> ion in oxidising flame is: [P.M.T. (Manipal) 2001]  (a) Cu $\Box$ (b) CuBO <sub>2</sub> $\Box$	64.	[A.I.E.E. 2002]  (a) HgS $\Box$ (b) HgS + Hg <sub>2</sub> S $\Box$ (c) HgS + Hg $\Box$ (d) Hg <sub>2</sub> S $\Box$ How do we differentiate between Fe <sup>3+</sup> and Cr <sup>3+</sup> in group III?  [A.I.E.E. 2002]  (a) By adding excess of NH <sub>4</sub> OH solution  (b) By increasing NH <sub>4</sub> ion concentration  (c) By decreasing OH ion concentration
53.	solubility in water? [A.I.I.M.S. 2001]  (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001]  (a) Deliquescence $\Box$ (b) Efflorescence $\Box$ (c) Allotropy $\Box$ (d) Sublimation $\Box$ The compound formed in the borax bead test of Cu <sup>2+</sup> ion in oxidising flame is: [P.M.T. (Manipal) 2001]  (a) Cu $\Box$ (b) CuBO <sub>2</sub> $\Box$ (c) Cu(BO <sub>2</sub> ) <sub>2</sub> $\Box$ (d) none of these	64.	[A.I.E.E. 2002]  (a) HgS $\square$ (b) HgS + Hg <sub>2</sub> S $\square$ (c) HgS + Hg $\square$ (d) Hg <sub>2</sub> S $\square$ How do we differentiate between Fe <sup>3+</sup> and Cr <sup>3+</sup> in group III?  [A.I.E.E. 2002]  (a) By adding excess of NH <sub>4</sub> OH solution  (b) By increasing NH <sub>4</sub> ion concentration  (c) By decreasing OH ion concentration  (d) Both (b) and (c)
53.	solubility in water? [A.I.I.M.S. 2001]  (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001]  (a) Deliquescence $\Box$ (b) Efflorescence $\Box$ (c) Allotropy $\Box$ (d) Sublimation $\Box$ The compound formed in the borax bead test of Cu <sup>2+</sup> ion in oxidising flame is: [P.M.T. (Manipal) 2001]  (a) Cu $\Box$ (b) CuBO <sub>2</sub> $\Box$	64.	[A.I.E.E. 2002]  (a) HgS $\Box$ (b) HgS + Hg <sub>2</sub> S $\Box$ (c) HgS + Hg $\Box$ (d) Hg <sub>2</sub> S $\Box$ How do we differentiate between Fe <sup>3+</sup> and Cr <sup>3+</sup> in group III?  [A.I.E.E. 2002]  (a) By adding excess of NH <sub>4</sub> OH solution  (b) By increasing NH <sub>4</sub> <sup>+</sup> ion concentration  (c) By decreasing OH ion concentration  (d) Both (b) and (c) $\Box$ In Nessler's reagent for detection of ammonia, the active species is: [P.M.T. (Kerala) 2003]
53. 54.	solubility in water? [A.I.I.M.S. 2001]  (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001]  (a) Deliquescence $\Box$ (b) Efflorescence $\Box$ (c) Allotropy $\Box$ (d) Sublimation $\Box$ The compound formed in the borax bead test of Cu <sup>2+</sup> ion in oxidising flame is: [P.M.T. (Manipal) 2001]  (a) Cu $\Box$ (b) CuBO <sub>2</sub> $\Box$ (c) Cu(BO <sub>2</sub> ) <sub>2</sub> $\Box$ (d) none of these	64.	[A.I.E.E. 2002]  (a) HgS $\Box$ (b) HgS + Hg <sub>2</sub> S $\Box$ (c) HgS + Hg $\Box$ (d) Hg <sub>2</sub> S $\Box$ How do we differentiate between Fe <sup>3+</sup> and Cr <sup>3+</sup> in group III?  [A.I.E.E. 2002]  (a) By adding excess of NH <sub>4</sub> OH solution  (b) By increasing NH <sub>4</sub> <sup>+</sup> ion concentration  (c) By decreasing OH ion concentration  (d) Both (b) and (c) $\Box$ In Nessler's reagent for detection of ammonia, the active species is:  [P.M.T. (Kerala) 2003]  (a) Hg <sub>2</sub> Cl <sub>2</sub> $\Box$ (b) Hg <sup>2+</sup> $\Box$
53. 54.	solubility in water? [A.I.I.M.S. 2001]  (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001]  (a) Deliquescence $\Box$ (b) Efflorescence $\Box$ (c) Allotropy $\Box$ (d) Sublimation $\Box$ The compound formed in the borax bead test of Cu <sup>2+</sup> ion in oxidising flame is: [P.M.T. (Manipal) 2001]  (a) Cu $\Box$ (b) CuBO <sub>2</sub> $\Box$ (c) Cu(BO <sub>2</sub> ) <sub>2</sub> $\Box$ (d) none of these $\Box$ A gas 'X' is passed through water to form a saturated	64.	[A.I.E.E. 2002]  (a) HgS $\square$ (b) HgS + Hg <sub>2</sub> S $\square$ (c) HgS + Hg $\square$ (d) Hg <sub>2</sub> S $\square$ How do we differentiate between Fe <sup>3+</sup> and Cr <sup>3+</sup> in group III?  [A.I.E.E. 2002]  (a) By adding excess of NH <sub>4</sub> OH solution  (b) By increasing NH <sub>4</sub> <sup>+</sup> ion concentration  (c) By decreasing OH ion concentration  (d) Both (b) and (c) $\square$ In Nessler's reagent for detection of ammonia, the active species is:  [P.M.T. (Kerala) 2003]  (a) Hg <sub>2</sub> Cl <sub>2</sub> $\square$ (b) Hg <sup>2+</sup> $\square$ (c) Hg <sub>2</sub> I <sub>2</sub> $\square$ (d) HgI <sub>4</sub> <sup>2-</sup> $\square$
53. 54.	solubility in water? [A.I.I.M.S. 2001]  (a) HgS $K_{sp} = 10^{-54}$ $\Box$ (b) CdS $K_{sp} = 10^{-30}$ $\Box$ (c) FeS $K_{sp} = 10^{-20}$ $\Box$ (d) ZnS $K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001]  (a) Deliquescence $\Box$ (b) Efflorescence $\Box$ (c) Allotropy $\Box$ (d) Sublimation $\Box$ The compound formed in the borax bead test of Cu <sup>2+</sup> ion in oxidising flame is: [P.M.T. (Manipal) 2001]  (a) Cu $\Box$ (b) CuBO <sub>2</sub> $\Box$ (c) Cu(BO <sub>2</sub> ) <sub>2</sub> $\Box$ (d) none of these $\Box$ A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with the AgNO <sub>3</sub>	64.	[A.I.E.E. 2002]  (a) HgS $\square$ (b) HgS + Hg <sub>2</sub> S $\square$ (c) HgS + Hg $\square$ (d) Hg <sub>2</sub> S $\square$ How do we differentiate between Fe <sup>3+</sup> and Cr <sup>3+</sup> in group III?  [A.I.E.E. 2002]  (a) By adding excess of NH <sub>4</sub> OH solution $\square$ (b) By increasing NH <sub>4</sub> <sup>+</sup> ion concentration $\square$ (c) By decreasing OH ion concentration $\square$ (d) Both (b) and (c) $\square$ In Nessler's reagent for detection of ammonia, the active species is: [P.M.T. (Kerala) 2003]  (a) Hg <sub>2</sub> Cl <sub>2</sub> $\square$ (b) Hg <sup>2+</sup> $\square$ (c) Hg <sub>2</sub> I <sub>2</sub> $\square$ (d) HgI <sub>4</sub> <sup>2-</sup> $\square$ (e) Hg <sub>2</sub> I <sup>2-</sup> $\square$
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<ul><li>53.</li><li>54.</li><li>55.</li><li>56.</li></ul>	solubility in water? [A.I.I.M.S. 2001]  (a) $HgS K_{sp} = 10^{-54}$ $\Box$ (b) $CdS K_{sp} = 10^{-30}$ $\Box$ (c) $FeS K_{sp} = 10^{-20}$ $\Box$ (d) $ZnS K_{sp} = 10^{-22}$ $\Box$ The phenomenon in which white transparent crystal changes into white powder is called: [A.I.I.M.S. 2001]  (a) Deliquescence $\Box$ (b) Efflorescence $\Box$ (c) Allotropy $\Box$ (d) Sublimation $\Box$ The compound formed in the borax bead test of $Cu^{2+}$ ion in oxidising flame is: [P.M.T. (Manipal) 2001]  (a) $Cu$ $\Box$ (b) $CuBO_2$ $\Box$ (c) $Cu(BO_2)_2$ $\Box$ (d) none of these $\Box$ A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with the AgNO3 gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y': [I.I.T. (S) 2001]  (a) $X = CO_2$ , $Y = Cl_2$ $\Box$ (b) $X = Cl_2$ , $Y = CO_2$ $\Box$ (c) $X = Cl_2$ , $Y = H_2$ $\Box$ (d) $X = H_2$ , $Y = Cl_2$ $\Box$ An aqueous solution of a substance gives a white precipitate on treatment with dil. HCl which dissolves on heating. When $H_2S$ is passed through the hot acidic solution, a black precipitate is obtained. The substance is: [I.I.T. (S) 2002]  (a) $Hg_2^{2+}$ salt $\Box$ (b) $Cu^{2+}$ salt $\Box$ (c) $Ag^+$ salt $\Box$ (d) $Ag^+$ salt $\Box$ (d) $Ag^+$ salt $\Box$ (e) $Ag^+$ salt $\Box$ (d) $Ag^+$ salt $\Box$ (e) $Ag^+$ salt $\Box$ (f) $Ag^+$ salt $\Box$ (f) $Ag^+$ salt $\Box$	64.	[A.I.E.E. 2002]  (a) HgS
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68.	tube, results in liberation of some violet coloured fumes and droplets of a metal appear on cooler part of the test tube. The red solid is:   [A.I.E.E.E. 2003]  (a) $Pb_3O_4$ (b) $HgI_2$ (c) $HgO$ (d) $(NH_4)_2Cr_2O_7$ Which of the following is false ?	77. 78.	To a metal nitrate, when KI solution is added, a black precipitate is produced at first, on adding excess of KI orange solution is produced. Identify the metal ion: [1.I.T. 2005]  (a) $Hg^{2+}$ $\Box$ (b) $Bi^{3+}$ $\Box$ (c) $Cu^{2+}$ $\Box$ (d) $Pb^{2+}$ $\Box$ When calomel reacts with $NH_4OH$ solution, the compound
	<ul> <li>(a) In Vth group, K<sub>2</sub>CrO<sub>4</sub> is used for the test of Ba<sup>2+</sup> □</li> <li>(b) Ammonium sulphate can be used in place of NH<sub>4</sub>Cl in IIIrd group □</li> </ul>		formed is: [B.C.E.C.E. (Medical) 2005] (a) $NH_2(Hg)Cl$ $\Box$ (b) $Hg_2Cl_2NH_3$ $\Box$ (c) $Hg(NH_3)_2Cl_2$ $\Box$ (d) $HgCl_2NH_3$ $\Box$
	(c) Lime water is used for the test of $CO_3^{2-}$ . $\Box$ (d) Ammonium thiocyanate can be used in the detection of $CO_3^{2+}$ and $CO_3^{2+}$ $\Box$	79.	The brown ring test for nitrates depends on:  (a) the reduction of nitrate to nitric oxide
69.	$Co^{2+}$ and $Fe^{3+}$ ions $\Box$ When $H_2S$ gas is passed in a metal sulphate solution in presence of NH <sub>4</sub> OH, a white precipitate is produced. The	,	(b) oxidation of nitric oxide to nitrogen dioxide (c) reduction of ferrous sulphate to iron (d) oxidising action of sulphuric acid  □
	metal is identified as: [C.P.M.T. 2003] (a) Zn $\square$ (b) Fe $\square$	80.	The formula of the compound which gives violet colour in Lassaigne's test for sulphur with sodium nitroprusside is:
	(c) Pb (d) Hg		[P.M.T. (Kerala) 2006]
70.	In the test for iodine, when $I_2$ is treated with sodium thiosulphate, $Na_2S_2O_3$ :		(a) $Na_4[Fe(CN)_6S]$ $\square$ (b) $Na_4[Fe(CN)_5NCS]$ $\square$ (c) $Na_4[Fe(CN)_5NOS]$ $\square$ (d) $Na_2[Fe(CN)_5NOS]$ $\square$
	$Na_2S_2O_3 + I_2 \longrightarrow NaI +$ [B.H.U. 2003]	81.	MgSO <sub>4</sub> on reaction with NH <sub>4</sub> OH and Na <sub>2</sub> HPO <sub>4</sub> forms a white
	(a) $Na_2S_4O_6$ $\square$ (b) $Na_2SO_4$ $\square$		crystalline precipitate. What is its formula? [I.I.T. 2006]
	(c) $Na_2S$ $\square$ (d) $Na_3ISO_4$ $\square$		(a) $Mg(NH_4)PO_4$ $\square$ (b) $Mg_3(PO_4)_2$ $\square$
71.	Which of the following sulphides is yellow in colour?		(c) $MgCl_2 \cdot MgSO_4$
/1.	[P.M.T.(M.P.) 2005]	1	[Hint: $MgSO_4 + NH_4OH + Na_2HPO_4 \longrightarrow$
	(a) CuS		$Mg(NH_4)PO_4 + Na_2SO_4 + H_2O$
	(c) $ZnS$ $\Box$ (d) $CoS$ $\Box$		(white ppt.)
72.	Brown ring in the test of $NO_3^-$ is formed due to the formation	82.	A solution when diluted with water and boiled, gives a white
1 2000	of: [P.M.T.(M.P.) 2005]		precipitate. On addition of excess of NH <sub>4</sub> Cl/NH <sub>4</sub> OH, the
	(a) FeSO <sub>4</sub> ·NO		volume of precipitate decreases leaving behind a white
	(c) $Fe_2(SO_4)_3$ NO $\Box$ (d) none of these $\Box$		gelatinous precipitate. Identify the precipitate which
72			dissolves in NH <sub>4</sub> OH/NH <sub>4</sub> Cl: [I.I.T. 2006]
73.			(a) $Zn(OH)_2$ $\Box$ (b) $Al(OH)_3$ $\Box$
	by $H_2S$ gas in the presence of $NH_3$ ? [Jamia 2004] (a) $Mn^{2+}$ $\square$ (b) $Ni^{2+}$ $\square$		(c) $Mg(OH)_2$ $\square$ (d) $Ca(OH)_2$ $\square$
	2.		$[Hint]: Zn^{2+} + 4NH_4OH \longrightarrow [Zn(NH_3)_4]^{2+} + 4H_2O]$
71		83.	A sodium salt of unknown anion when treated with MgCl <sub>2</sub>
74.			gives white precipitate only on boiling. The anion is:
	[P.M.T.(Punjab) 2005]		[I.I.T. 2004]
	(a) $Fe(OH)_3$		(a) $SO_4^{2-}$
75.	(c) $Al(OH)_3$		$\square$ (c) $CO_3^{2-}$ $\square$ (d) $NO_3^ \square$
13.	Nessler's reagent is: [P.M.T.(Raj.) 2005]		[Hint: $MgCl_2 + 2NaHCO_3 \longrightarrow Mg(HCO_3)_2 \xrightarrow{Boil} MgCO_3$ ]
	(a) NaHgCl <sub>4</sub> $\square$ (b) K <sub>2</sub> HgI <sub>4</sub> $\square$	0.4	Soluble ppt.
	(c) $Hg(NH_3)_2Cl$ $\Box$ (d) $K_2HgI_4 + KOH$ $\Box$	84.	Iron is precipitated as Fe(OH) <sub>3</sub> in the third group and not as
76.	If Fe <sup>3+</sup> and Cr <sup>3+</sup> both are present in group III of qualitative	,	Fe(OH) <sub>2</sub> because:
	analysis, then distinction can be made by:		(a) Fe(OH) <sub>2</sub> is light green ☐ (b) Fe(OH) <sub>3</sub> is reddish brown ☐
	[Jamia(Engg.) 2005]		(c) Fe(OH) <sub>2</sub> is partially soluble and is not completely
	(a) addition of NH <sub>4</sub> OH in presence of NH <sub>4</sub> Cl, when only		precipitated
	Fe(OH) <sub>3</sub> is precipitated		(d) Fe(OH) <sub>2</sub> is oxidant
	(b) addition of NH <sub>4</sub> OH in presence of NH <sub>4</sub> Cl, when Cr(OH) <sub>3</sub>	85	From the following information,
	and Fe(OH) <sub>3</sub> both are precipitated and on adding Br <sub>2</sub> water and NaOH, Cr(OH) <sub>3</sub> dissolves	05.	$X + H_2SO_4 \longrightarrow Y$ (a colourless and irritating gas)
			$Y + K_2Cr_2O_7 + H_2SO_4 \longrightarrow $ (Green coloured solution)
	(c) precipitates of Cr(OH) <sub>3</sub> and Fe(OH) <sub>3</sub> as obtained in (b) are treated with conc. HCl, when only Fe(OH) <sub>3</sub> dissolves	Ì	Identify the pair $X$ and $Y$ from the list given below:
	are treated with conc. HCI, when only Fe(OH)3 dissolves		(a) CI, HCl $\Box$ (b) $S^2$ , $H_2S$ $\Box$
	(d) (b) and (c) both are correct		2
	(a) (b) and (c) boat are edited:	1	(c) $CO_3^{2-}$ , $CO_2$

6		
	[Hint: $SO_3^{2-} + H_2SO_4 \longrightarrow SO_4^{2-} + SO_2 + H_2O$	94. The brown ring test for nitrates depends on:
	$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O]$	[A.F.M.C. 2008]
	Green	(a) the reduction of nitrate to nitric oxide $\Box$
86.	$K_4$ Fe(CN) <sub>6</sub> is not used for the detection of:	(b) oxidation of nitric oxide to nitrogen dioxide $\Box$
	(a) $Zn^{2+}$ ions $\Box$ (b) $Cu^{2+}$ ions $\Box$	(c) reduction of ferrous sulphate to iron $\Box$
	(c) $Fe^{3+}$ ions $\Box$ (d) $Fe^{2+}$ ions $\Box$	(d) oxidising action of sulphuric acid $\Box$
07		95. $S^{2-}$ and $SO_3^{2-}$ can be distinguished by using:
87.	When H <sub>2</sub> S gas is passed through the HCl containing	[A.I.I.M.S. 2008]
	aqueous solution of CuCl <sub>2</sub> , HgCl <sub>2</sub> , BiCl <sub>3</sub> and CoCl <sub>2</sub> , it does	(a) $(CH_3COO)_2Pb$ $\Box$ (b) $Na_2[Fe(CN)_5NO]$ $\Box$
	not precipitate out: [A.I.I.M.S. 2007] (a) CuS	(c) both (a) and (b) $\Box$ (d) none of these $\Box$
	_ (-)8	96. In which of the following ammonia is not used?
00	( ) 2 3	[C.E.T. (Karnataka) 2009]
88.	A metal salt solution forms a yellow precipitate with sodium chromate solution and a white precipitate with sodium	(a) Nessler's reagent
	sulphate solution. However, it gives no precipitate with	(b) group reagent for analysis of IVth group basic radicals
	sodium chloride or iodide solution. The metal salt is:	
	(a) $Pb(NO_3)_2$ $\Box$ (b) $Ba(NO_3)_2$ $\Box$	(c) group reagent for analysis of IIIrd group basic radicals
	(a) $FO(NO_3)_2$	
89.	A certain light green salt gives ammonia on heating with	(d) Tollens reagent
67.	NaOH solution. Its aqueous solution gives white precipitate	97. The incorrect statement in respect of chromyl chloride test
	with barium chloride solution. Aqueous solution also shows	is: [C.E.T. (Karnataka) 2009]
	the presence of Fe(II) ion. The salt is likely to be:	(a) formation of lead chromate
	(a) ferrous sulphate $\Box$ (b) Mohr's salt $\Box$	(b) formation of chromyl chloride
	(c) ferric alum	(c) liberation of chloride
90.	A solution of a metal ion when treated with KI gives a red	(d) formation of red vapours
	precipitate which dissolves in excess of KI to give a	98. Out of Cu <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> and Mn <sup>2+</sup> those dissolve in dil. HCl
	colourless solution. Moreover, the solution of metal ion on	only one gives a precipitate when H <sub>2</sub> S is passed. Identify
	treatment with a solution of cobalt(II)thiocyanate gives rise	the corresponding one: [J.E.E. (Orissa) 2009]
	to deep blue crystalline precipitate. The metal ion is:	(a) $Ni^{2+}$ $\Box$ (b) $Cu^{2+}$ $\Box$
	[L.I.T. 2007]	(c) $\operatorname{Co}^{2+}$ $\square$ (d) $\operatorname{Mn}^{2+}$ $\square$
	(a) $Pb^{2+}$ $\Box$ (b) $Hg^{2+}$ $\Box$	99. A white crystalline salt A reacts with dilute HCl to liberate a
	(a) $Pb^{2+}$ $\square$ (b) $Hg^{2+}$ $\square$ (c) $Cu^{2+}$ $\square$ (d) $Co^{2+}$ $\square$	suffocating gas B and also forms a yellow precipitate. The
		gas B turns potassium dichromate acidified with dilute H <sub>2</sub> SO <sub>4</sub>
	[Hint: $Hg^{2+} + 2I^{-} \longrightarrow HgI_{2}$ Red upt.	to a green coloured solution C. A, B and C are respectively:
	11	[C.E.T. (Karnataka) 2010]
	$HgI_2 + 2KI \longrightarrow K_2HgI_4$ Soluble	(a) $Na_2SO_3$ , $SO_2$ , $Cr_2(SO_4)_3$
		(b) $Na_2S_2O_3$ , $SO_2$ , $Cr_2(SO_4)_3$
	$Hg^{2+} + Co(SCN)_2 \longrightarrow Co[Hg(SCN)_4]$ ] Deep blue ppt.	(c) $Na_2S$ , $SO_2$ , $Cr_2(SO_4)_3$
<b>Q</b> 1	In the brown ring test, the brown colour of the ring is due	(d) $Na_2SO_4$ , $SO_2$ , $Cr_2(SO_4)_3$
<i>)</i> 1.	to: [C.E.T. (Karnataka) 2008]	[ <b>Hint</b> : $Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + S + H_2O$
	(a) a mixture of NO and NO <sub>2</sub> $\Box$	(A) (B) Yellow ppt.
	(b) nitrosoferrous sulphate	
	(c) ferrous nitrate	$ K_2 \operatorname{Cr}_2 \operatorname{O}_7 + H_2 \operatorname{SO}_4 + \operatorname{SO}_2 \longrightarrow \operatorname{Cr}_2 (\operatorname{SO}_4)_3 ] $ (C)
	(d) ferric nitrate	
92.	When KI is added to acidified solution of sodium nitrite:	$100. A + CH3COOH \longrightarrow B + CO2 + H2O$ Soluble
	[J.E.E. (W.B.) 2008]	
	(a) NO gas is liberated and I <sub>2</sub> is set free	$B + (NH_4)_2 C_2 O_4 \longrightarrow White ppt.$
	(b) $N_2$ gas is liberated and HI is produced	A and B may contain:
	(c) $N_2O$ gas is liberated and $I_2$ is set free $\square$	(a) $Ni^{2+}$
	(d) $N_2$ gas is liberated and HOI is produced	
	[Hint: $2I^- + 4H^+ + 2NO_2^- \longrightarrow 2NO + I_2 + 2H_2O$ ]	[Hint: $CaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + CO_2 + H_2O$
93.		(A) (B)
	[J.E.E. (W.B.) 2008]	$Ca(CH_3COO)_2 + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4 + 2CH_3COONH_4$
	(a) NaCl solution	White ppt.
	(a) NaOU solution	

Ansu	vers =								
<b>1.</b> (b)	<b>2.</b> (c)	<b>3.</b> (d)	<b>4.</b> (a)	5. (b)	<b>6.</b> (a)	7. (c)	<b>8.</b> (d)	9. (a)	<b>10.</b> (b)
<b>11.</b> (b)	<b>12.</b> (c)	<b>13.</b> (d)	<b>14.</b> (a)	<b>15.</b> (b)	<b>16.</b> (b)	17. (c)	<b>18.</b> (b)	<b>19.</b> (a)	<b>20.</b> (d)
<b>21.</b> (b)	<b>22.</b> (a)	<b>23.</b> (b)	<b>24.</b> (a)	<b>25.</b> (d)	<b>26.</b> (c)	<b>27.</b> (b)	<b>28.</b> (c)	<b>29.</b> (d)	<b>30.</b> (d)
<b>31.</b> (a)	<b>32.</b> (b)	<b>33.</b> (c)	<b>34.</b> (b)	35. (d)	<b>36.</b> (b)	<b>37.</b> (c)	<b>38.</b> (c)	<b>39.</b> (a)	<b>40.</b> (b)
<b>41.</b> (a)	<b>42.</b> (b)	<b>43.</b> (c)	<b>44.</b> (d)	<b>45.</b> (a)	<b>46.</b> (c)	<b>47.</b> (c)	<b>48.</b> (b)	<b>49.</b> (b)	<b>50.</b> (d)
<b>51.</b> (c)	<b>52.</b> (c)	<b>53.</b> (b)	<b>54.</b> (c)	<b>55.</b> (c)	<b>56.</b> (d)	<b>57.</b> (d)	<b>58.</b> (d)	<b>59.</b> (b)	<b>60.</b> (d)
<b>61.</b> (b)	<b>62.</b> (c)	<b>63.</b> (c)	<b>64.</b> (d)	<b>65.</b> (d)	<b>66.</b> (b)	<b>67.</b> (b)	<b>68.</b> (b)	<b>69.</b> (a)	<b>70.</b> (a)
<b>71.</b> (b)	72. (a)	<b>73.</b> (d)	<b>74.</b> (a)	<b>75.</b> (b)	<b>76.</b> (b)	<b>77.</b> (b)	<b>78.</b> (a)	<b>79.</b> (a)	<b>80.</b> (c)
<b>81.</b> (a)	<b>82.</b> (a)	<b>83.</b> (b)	<b>84.</b> (c)	<b>85.</b> (d)	<b>86.</b> (d)	<b>87.</b> (d)	<b>88.</b> (b)	<b>89.</b> (b)	<b>90.</b> (b)
<b>91.</b> (b)	<b>92.</b> (a)	<b>93.</b> (c)	<b>94.</b> (a)	<b>95.</b> (c)	<b>96.</b> (a)	<b>97.</b> (c)	<b>98.</b> (b)	<b>99.</b> (b)	<b>100.</b> (d)

 $\begin{array}{c} \text{Ca(OH)}_2 \, + \, \text{CO}_2 \longrightarrow \begin{array}{c} \text{CaCO}_3 \, + \, \text{H}_2\text{O} \end{array} ] \\ \text{Milkiness} \end{array}$ 



### **Objective Questions for IIT ASPIRANTS**



		-	
1.	Which of the following pairs of ions would be expected to	13.	$[X] + H_2SO_4 \longrightarrow [Y]$ a colourless gas with irritating smell,
	form precipitate when their dilute solutions are mixed?		$[Y] + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$ Green solution. [X] and [Y] are:
	(a) $Na^+$ , $SO_3^{2-}$ (b) $NH_4^+$ , $CO_3^{2-}$		(a) $SO_3^{2-}$ and $SO_2$ (b) $Cl^-$ and $HCl$
	(c) $Na^+, S^{2-}$ (d) $Fe^{3+}, PO_4^{3-}$		(c) $S^2$ and $H_2S$ (d) $CO_2^3$ and $CO_2$
2.	An orange precipitate in the second group is given by:	1.1	
	(a) $Sb^{3+}$ (b) $Sn^{2+}$ .	14.	An aqueous solution containing Hg <sup>2+</sup> , Hg <sup>2+</sup> , Pb <sup>2+</sup> and Cd <sup>2+</sup>
		\ .	ions will give precipitates of with HCl.
	(c) $Hg^{2+}$ (d) $As^{3+}$	\ <u>'</u>	(a) Hg <sub>2</sub> Cl <sub>2</sub> only (b) PbCl <sub>2</sub> only (c) Hg <sub>2</sub> Cl <sub>2</sub> and PbCl <sub>2</sub> (d) HgCl <sub>2</sub> and PbCl <sub>2</sub>
3.	$Mn^{2+} + PbO_2 \xrightarrow{conc. HNO_3} $ light purple coloured solution	15	A solution of salt/salts in HCl when diluted with water turns
	contains:	13.	milky. It indicates the presence of:
	(a) $HMnO_4$ (b) $Pb(NO_3)_2$		(a) Sn salt (b) Bi salt
*	(c) $Mn(NO_3)_2$ (d) $H_2MnO_4$		(c) Sb salt (d) Cu salt
. (	Fused with $Na_2CO_3$ (H <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O)	16	Ammonium salt gives brown colour with alkaline solution of
4.	$(A) \xrightarrow{\text{Fused with Na}_2\text{CO}_3} (B) \xrightarrow{\text{(H}_2\text{SO}_4 + \text{H}_2\text{O})} (C)$ Green solid Yellow Orange		Nessler's reagent to form iodide of Millon's base. The formula
	solution Tellow		of this compound is:
	(CH <sub>3</sub> COO) <sub>2</sub> Pb		(a) NH <sub>2</sub> —Hg—O—Hg—I (b) NH <sub>2</sub> —O—Hg—HgI
	(D) Yellow ppt.		(c) $K_2HgI_4$ (d) $NH_2-Hg-I$
	Here, $A$ , $B$ , $C$ and $D$ are respectively:	17.	H <sub>2</sub> S gas is passed into zinc acetate and zinc chloride
	A' , $B$ $C$ $D$	_	solutions in separate test tubes (I) and (II). The ZnS is
	(a) FeSO <sub>4</sub> FeCO <sub>3</sub> Fe(OH) <sub>3</sub> PbCO <sub>3</sub>		precipitated in:
	(b) Cr <sub>2</sub> O <sub>3</sub> Na <sub>2</sub> CrO <sub>4</sub> Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> PbCrO <sub>4</sub>		(a) (I) (b) (II)
	(c) FeCl <sub>2</sub> FeSO <sub>4</sub> PbSO <sub>4</sub> Fe(OH) <sub>3</sub>		(c) both (d) none of these
	(d) FeSO <sub>4</sub> FeCl <sub>3</sub> Fe(OH) <sub>3</sub> PbCl <sub>2</sub>		[Hint: ZnS is precipitated in weak acid or alkaline solution.]
5.		18.	Which give/gives a black precipitate when H <sub>2</sub> S is passed
	on heating?		through an acidic solution of ?
	(a) CuCO <sub>3</sub> (b) Ag <sub>2</sub> CO <sub>3</sub>		(a) Nickel acetate . (b) Copper acetate
	(c) $Na_2CO_3$ (d) $MgCO_3$	•	(c) Cobalt acetate (d) Lead acetate
6.	The sulphide, which is insoluble in 50% HNO <sub>3</sub> is:	<b>19.</b>	Which of the following ions can be detected by flame test?
	(a) HgS (b) CuS	•	(a) $K^{+}$ (b) $Ba^{2+}$
•	(c) Bi <sub>2</sub> S <sub>3</sub> (d) PbS		(c) $Ca^{2+}$ (d) $Mg^{2+}$
7.	The ions which can be precipitated with both HCl and H <sub>2</sub> S.	20.	,,
	are:		(a) $Mg^{2+}$ (b) $Mn^{2+}$
• '	(a) $Pb^{2+}$ (b) $Cu^{2+}$		(c) $Cu^{2+}$ (d) $Pb^{2+}$
	(c) $Ag^+$ (d) $Sn^{2+}$	21.	A colourless salt 'A' $\xrightarrow{\text{MnO}_4^-/\text{H}^+}$ Decolourisation of
8.	Which of the following are soluble in water?	,	permanganate solution occurs
	(a) $CaC_2O_4$ (b) $SrSO_4$		permanganate solution occurs
	(c) $BaCl_2$ (d) $(NH_4)_2C_2O_4$	•	$\xrightarrow{\text{Heat}} X + Y + Z;  Z \xrightarrow{\text{H}_2\text{O}} B'$
9.	Salt of which of the following radicals will give brown fumes		
	when treated with conc. HNO <sub>3</sub> ?		Gases
	(a) $NO_3^-$ (b) Br		Gas $Y \rightarrow B \longrightarrow Milkiness$
	(c) $\Gamma$ (d) $Cl^-$		Gas X burns with blue flame. Mark the correct choice.
10.	Which of the following halides are not soluble in water?		$A \qquad X \qquad Y \qquad Z \qquad B$
	(a) AgCl (b) AgBr		(a) $CaCO_3$ CO $CO_2$ CaO $Ca(OH)_2$
	(c) PbCl <sub>2</sub> (d) AgF		(b) $CaC_2O_4$ CO $CO_2$ CaO $Ca(OH)_2$
11.	Aqueous solution of KI is used to detect:		(c) CaC <sub>2</sub> O <sub>4</sub> CO <sub>2</sub> CO CaO Ca(OH) <sub>2</sub>
	(a) $Hg^{2+}$ (b) $Pb^{2+}$		(d) $CaOCl_2$ $Cl_2$ $O_2$ $CaO$ $Ca(OH)_2$
10	(c) $Ag^+$ (d) $Be^{3+}$		[Hint: $CaC_2O_4 \longrightarrow CO + CO_2 + CaO$ ;
12.	Potassium chromate ( $K_2CrO_4$ ) is used to identify:		$(A) \qquad (X)  (Y)  (Z)$
	(a) $Pb^{2+}$ (b) $Ba^{2+}$ (c) $Aa^{+}$ (d) $Ca^{2+}$		$CaO + H_2O \longrightarrow Ca(OH)_2$
	101 A II		(T)

22. Conc. H2SO4 Brown fumes Colourless salt 'A' Blue solution + metal 'C' White ppt. soluble in NH<sub>4</sub>OH The salt 'A' is: (a)  $Cu(NO_3)_2$ (b) Pb(NO<sub>3</sub>)<sub>2</sub> (c) AgNO<sub>3</sub> (d)  $Zn(NO_3)_2$ [Hint:  $2AgNO_3 + H_2SO_4 \rightarrow Ag_2SO_4 + 2NO_2 + H_2O + \frac{1}{2}O_2$  $2AgNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2Ag$ 3. (a) 4. (b) 5. (b,c) **6.** (a)

 $AgNO_3 + HCl \longrightarrow AgCl + HNO_3$ White ppt. soluble in NH4OH 23. NaCl +  $K_2Cr_2O_7$  + Conc.  $H_2SO_4 \xrightarrow{\text{Heat}}$  Red coloured gas  $X \leftarrow \frac{\text{CH}_3\text{COOH}}{\text{Pb}(\text{CH}_3\text{COO})_2} - \text{Yellow} \leftarrow \text{Solution}$ NaOH solution The formula and colour of X is: (a) CrO<sub>2</sub>Cl<sub>2</sub>, red (b)  $Cr_2(SO_4)_3$ , green (c) PbO, yellow (d) PbCrO<sub>4</sub>, vellow [Hint: Chromyl chloride test]

7. (a,c) 8. (c,d) **9.** (a,b) 10. (a,b,c)11. (a,b,c) 12. (a,b,c) 13. (a) 14. (c) 15. (a,b,c) 16. (a) **18.** (b,d) **19.** (a,b,c) **20.** (d) **21.** (b) **22.** (c) 23. (d) 17. (a)

Cu<sup>2+</sup>

### Matrix Matching Questions for IIT Aspirants

(a-s)

(a-p, q) (a-p, s) (b-r)

(b-s)

(b-r, s)

1. Match the reagents (List-II) with their uses (List-II):

List-I	List-II
(Reagents)	(Uses)
(a) Nessler's reagent	(p) Chromyl chloride test
(b) $K_2Cr_2O_7$	(q) Prussian blue test of Fe <sup>3</sup>
(c) NaOH	(r) Chocolate brown test of
(d) $K_4[Fe(CN)_6]$	(s) NH <sub>4</sub> ion
Motob the radicals of List I	with their groups of List II.

Match the radicals of List-I with their groups of List-II:

List-II List-I (a) Pb<sup>2+</sup> (p) Ist group (b) Cu<sup>2+</sup> (q) Zero group (c) NH<sub>4</sub><sup>+</sup> (r) 3rd group (d)  $Al^{3+}$ (s) 2nd group 3. Match the sulphates of List-I with their properties of List-II: List-I List-II (a) CuSO<sub>4</sub>·5H<sub>2</sub>O (p) Water insoluble

(c) BaSO<sub>4</sub> (r) Blue coloured (s) White residue (in solid state) (d)  $Ag_2SO_4$ Match the radicals of List-I with their group reagents of List-II: · List-II List-I

(q) Water soluble

(a) Pb<sup>2+</sup> (p) H<sub>2</sub>S (b) Co<sup>2+</sup>  $(q) (NH_4Cl + NH_4OH)$ (c)  $Fe^{3+}$ (r) HCl (d)  $Ba^{2+}$ (s)  $(NH_4)_2CO_3$ 

5. Match the metals in List-I with their flame colour in List-II:

#### List-I List-II (a) Lithium (p) Violet (b) Barium (q) Brick red (c) Calcium (r) Apple green (d) Magnesium (s) Crimson red (t) No flame colour

	(t) No name colour				
6.	Match the observations of List-I with inferences in List-II:				
	List-I	List-II			
*	(a) Canary yellow precipitate with ammonium molybdate.	(p) PO <sub>4</sub> <sup>3-</sup>			
	(b) Ring test (Brown)	(q) $As^{3+}$			
	(c) Acid radical decomposed	(r) NO <sub>3</sub>			
	by dil. H <sub>2</sub> SO <sub>4</sub>				
	(d) Acid radical decomposed	(s) NO <sub>2</sub>			
	by conc. H <sub>2</sub> SO <sub>4</sub>				
7.	Match List-I with List-II				
	List-I	List-II			
	(Sulphides)	(Colour/group)			
	(a) HgS	(p) 2nd group of basic radicals			
	(b) NiS	(q) Buff-colour			
	(c) MnS	(r) Dirty white			
	(d) ZnS	(s) Black			
		•.			
	•				
		•			

(c-q)

(c¬s)

(c-q)

(d-t)

(d-r, s)

(d-r)

(b) PbSO<sub>4</sub>

1.	(a-s)	(b-p)	(c-s)		$(\mathbf{d}-\mathbf{q}, \dot{\mathbf{r}})$	
2.	(a-p, s)	(b-s)	(c-q)	*	(d-r)	•
3.	(a-q, r)	(b-p, s)	(c-p, s)		(d-q, s)	,
4.	(a-p, r)	(b-q, p).	(c-q)		(d-q, s)	

# **Assertion-Reason Type Questions**

The following questions consist of two statements as Assertion (A) and Reason (R). While answering these questions choose correctly any one of the following responses.

- (a) If both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) If (A) is true but (R) is false.
- (d) If (A) is false but (R) is true.
- (e) If both (A) and (R) are false.
- 1. (A) CdS and As<sub>2</sub>S<sub>3</sub> both have yellow colour and precipitated by passing H<sub>2</sub>S through solution in dilute HCl.
  - (R) Both can be separated by yellow ammonium sulphide.
- 2. (A) Sulphur dioxide turns acidified potassium dichromate solution green.
  - (R) Sulphur dioxide is a reducing agent. It reduces acidified potassium dichromate into chromic compound which is green in colour.
- (A) Original solution for basic radicals can be prepared in concentrated HNO<sub>3</sub> or concentrated H<sub>2</sub>SO<sub>4</sub>.

- (R) Both the acids dissolve majority of inorganic salts.
- (A) Ammonium salts evolve ammonia when heated with NaOH.
  - (R) Ammonium salts are soluble in water.
- 5. (A) Chloride is confirmed by chromyl chloride test.
  - (R) Chlorine is evolved when chloride is heated with conc. H<sub>2</sub>SO<sub>4</sub>.
- **6.** (A) PbCl<sub>2</sub> and Hg<sub>2</sub>Cl<sub>2</sub> precipitates can be separated by hot water.
  - (R) Aqueous solution of PbCl<sub>2</sub> gives yellow precipitate with K<sub>2</sub>CrO<sub>4</sub> solution.
- (A) When Cl<sub>2</sub> gas is passed into a mixture containing Br
  and I and CHCl<sub>3</sub>, I<sub>2</sub> (violet) first appears in CHCl<sub>3</sub> layer.
  - (R) In excess of Cl<sub>2</sub> gas, violet colour disappears and CHCl<sub>3</sub> layer becomes brown.
- 8. (A) When H<sub>2</sub>S gas is passed into aqueous solution of ZnCl<sub>2</sub>, white precipitate of ZnS appears.
  - (R) ZnS is insoluble in HCl.

### Answers

**1.** (b)

**2.** (a)

3. (e)

4. (b)

5. (c)

**6.** (b)

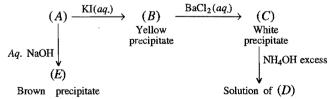
7. (a)

8. (e)

# THOUGHT TYPE QUESTIONS



#### **THOUGHT 1**



Answer the following questions:

- 1. Compound (A) is:
  - (a) CuSO<sub>4</sub>

- (b) AgNO<sub>3</sub>
- (c) Pb(NO<sub>3</sub>)<sub>2</sub>
- (d) Ca(NO<sub>3</sub>)<sub>2</sub>
- 2. Yellow precipitate (B) is:
  - (a) AgI

(b) PbI<sub>2</sub>

(c) Cal<sub>2</sub>

- (d) CH<sub>3</sub>I
- 3. White precipitate (C) obtained on treatment with aqueous solution of BaCl<sub>2</sub>, is:
  - (a) BaSO<sub>4</sub>
- (b) AgCl

(c) PbCl<sub>2</sub>

(d) CaCl<sub>2</sub>

- 4. The compound (D) obtained, when (C) dissolves in excess of NH<sub>4</sub>OH will be:
  - (a) AgOH

(b) [Ag(NH<sub>3</sub>)<sub>2</sub>Cl]

(c) Ag<sub>2</sub>O

- (d) AgNO<sub>3</sub>
- 5. Molecular formula of the compound 'E'; is:
  - (a)  $Ag_2O$

(b)  $Pb(OH)_2$ 

(c) AgOH

(d) Ca(OH)<sub>2</sub>

#### **THOUGHT 2**

A bluish green coloured compound (A), on thermal decomposition gives two products (B) and (C). When  $H_2$  gas is passed through (B) under hot conditions then a metal (D) is obtained. Both (A) and (B) are insoluble in water. Compound (B) is black coloured and gives chocolate brown precipitate (E) on treatment with  $K_4[Fe(CN)_6]$ . Compound (C) is colourless, odourless gas and it turns limewater milky.

Indicate whether following statements are true or false:

- 1. Compound (A) is CuCO<sub>3</sub>:
  - (a) True

(b) False

2. The black salt (B) is PbS:

(a) True

(b) False

3. The gaseous compound (C) is  $CO_2$ :

(a) True

(b) False

**4.** The metallic element (D) is copper:

(a) True

(b) False

5. The chocolate brown precipitate (E) is of  $Fe_4[Fe(CN)_6]_3$ :

(b) False

#### THOUGHT 3

A mixture contains four gases CO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub> and O<sub>2</sub>. Following four reagents are given for the detection of these gases:

- (a) Lime water
- (b) Acidified potassium dichromate
- (c) Pyrogallol
- (d) Turpentine oil

- 1. Which of the following gases will turn limewater milky?
  - (a) CO<sub>2</sub>

(b) SO<sub>2</sub>

(c)  $O_2$ 

(d)  $O_3$ 

Which of the following gases will turn acidified potassium dichromate green?

(a)  $CO_2$ 

(b) SO<sub>2</sub>

(c) O<sub>2</sub>

(d) O<sub>2</sub>

3. The gas which is absorbed in pyrogallol, is:

(a)  $CO_2$ 

(b) SO<sub>2</sub>

(c) O<sub>2</sub>

(d) O<sub>3</sub>

4. The gas which is absorbed in turpentine oil, is:

(a) CO<sub>2</sub>

(b) SO<sub>2</sub>

(c) O<sub>2</sub>

(d) O<sub>3</sub> 5. The gas which developes cracks in rubber, is:

(a) O<sub>2</sub>

(b) O<sub>2</sub>

(c) CO<sub>2</sub>

(d) SO<sub>2</sub>

### tuswers

Thought 1 1. (b) Thought 2 1. (a)

2. (b) 2. (b)

3. (b) 3. (a) 4. (b)

5. (c) 5. (b) 4- (a)

Thought 3 1. (a,b)

**2.** (b)

3. (c)

**4.** (d) **5.** (b)

## 

### BRAIN STORMING PROBLEMS



1. A mineral 'A' gave following reactions. Identify the compounds 'A' to 'H' on the basis of road map.

$$A'$$
  $\xrightarrow{\text{Dil.H}_2\text{SO}_4}$   $B'$  +  $C'$  + a gas  $D'$ 

 $(CH_3COO)_2Pb + 'D' \longrightarrow Black precipitate$ 

 $B' + C' \xrightarrow{D'} E'$  (another black precipitate)

('C' remains unaffected)

 $E' + HNO_3 \xrightarrow{\Delta} F'$  blue coloured solution

 $F' + K_4[Fe(CN)_6] \longrightarrow Chocolate brown precipitate$ 

 $C' + K_3 Fe(CN)_6 \longrightarrow H'$  blue coloured

[Ans.  $A: CuFeS_2, B: CuSO_4, C: FeSO_4,$ 

 $D: H_2S, E: CuS, F: Cu(NO_3)_2, G: Cu_2 [Fe(CN)_6]$ 

 $H: KFe[Fe(CN)_6] \rightarrow Turnbull's blue]$ 

2. A gas 'X' occupies 22.4 litre at S.T.P., its weight is 64 g. The gas turns acidified K2Cr2O7 green and decolourise acidified KMnO<sub>4</sub> solution. White turbidity appears when H<sub>2</sub>S gas is passed through aqueous solution of gas. What is the gas 'X'? Explain the reactions involved.

[Ans. SO<sub>2</sub>]

Hint:

(i)  $K_2Cr_2O_7 + H_2SO_4 + SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$ 

(ii)  $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$  $5SO_2 + 5H_2O + 5[O] \longrightarrow 5H_2SO_4$ 

 $2KMnO_4 + 3H_2SO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 5H_2SO_4$ 

(iii) 
$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$
 ]  
(White turbidity)

3. Aqueous solution of salt 'A' gives white precipitate of 'B' with NaCl solution. The filtrate gives black precipitate 'C' on passing H<sub>2</sub>S gas through it. Compound 'B' dissolves in hot water and the solution gives yellow precipitate 'D' on treatment with KI. Compound 'A' gives reddish brown fumes on heating. Identify the compounds 'A' to 'D'. [Ans. (A)  $Pb(NO_3)_2$ ; (B)  $PbCl_2$ ; (C) PbS; (D)  $PbI_2$ ]

4. 
$$[A]$$
  $\xrightarrow{KOH}$   $A$   $B$ 

Colourless Gas, giving white fumes with HCl

 $CaCl_2$ 
 $CaCl_2$ 

White precipitate, decolourises pink colour of acidified KMnO<sub>4</sub>.

What are [A], [B] and [C]? Give the reactions involved.

[Ans. (A)  $(NH_4)_2C_2O_4$ ; (B)  $NH_3$ ; (C)  $CaC_2O_4$ ]

[Hint: 
$$(NH_4)_2C_2O_4 + 2KOH \xrightarrow{\Delta} \begin{vmatrix} COOK \\ -\Delta \end{vmatrix} + 2NH_3 + 2H_2O$$

$$(NH_4)_2C_2O_4 + CaCl_2 \xrightarrow{CaC_2O_4} - 2NH_4Cl$$
White precipitate

$$CaC_2O_4 + H_2SO_4 \longrightarrow CaSO_4 + \begin{vmatrix} COOH \\ COOH \\ Oxalic acid \end{vmatrix}$$

$$CooH$$

$$Oxalic acid decolourises acidified KMnO_4.$$

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$COOH$$

$$5 \begin{vmatrix} +5[O] \longrightarrow 10CO_2 + 5H_2O \\ COOH \end{vmatrix}$$

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 \\ + 2MnSO_4 + 10CO_2 + 8H_2O_4 = 2MnSO_4 + 2MnSO_5 + 2MnS$$

- 5. An element 'A' on treatment with water evolves a colourless gas 'B' and gives a solution of 'C'. Lithium reacts with 'B' to form 'D'. Compound 'D' reacts with water to form a basic solution of 'E' and a gas 'F'. By passing CO<sub>2</sub> gas through the solution of 'C', it gives white precipitate of 'G' which dissolves in excess of CO<sub>2</sub> to form solution of 'H'. Precipitate 'G' gives deep red colour to the Bunsen burner flame. What are the compounds 'A' to 'H' and give the reactions involved?

  [Ans. (A) Ca; (B) H<sub>2</sub>; (C) Ca(OH)<sub>2</sub>; (D) LiH; (E) LiOH; (F) H<sub>2</sub>; (G) CaCO<sub>3</sub>; (H) Ca(HCO<sub>3</sub>)<sub>2</sub>]
- 6. A binary oxide (A) of alkaline earth metal when treated with HCl gives solid (B) and solution of (B). (B) gives apple green colour to the Bunsen flame. Solution of (C) decolourises acidified KMnO<sub>4</sub>. What are (A), (B) and (C)?

[Ans. (A) 
$$BaO_2$$
; (B)  $BaCl_2$ ; (C)  $H_2O_2$ ]

[Hint: 
$$BaO_2 + 2HCl \longrightarrow BaCl_2 + H_2O_2$$
(A)
(B)
(C)
$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$5H_2O_2 + 5[O] \longrightarrow 5H_2O + 5O_2$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

7. A colourless salt 'A' decolourises the pink colour of iodine. Solution of 'A' on treatment with AgNO<sub>3</sub> gives white precipitate. The compound 'A' turns FeCl<sub>3</sub> solution (yellow) to FeCl<sub>2</sub> solution (green). Identify 'A' and give the reactions involved.

[Ans. The compound 'A' is  $Na_2S_2O_3$ , i.e., sodium thiosulphate.] [Hint:  $2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$ 

$$Na_2S_2O_3 + 2AgNO_3 \longrightarrow 2NaNO_3 + Ag_2S_2O_3$$
  
White precipitate

$$2\text{FeCl}_3 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow 2\text{FeCl}_2 + \text{Na}_2\text{S}_4\text{O}_6 + 2\text{Na}^2\text{Cl}_2$$

8. Compound 'A' reduces HgCl<sub>2</sub> to a white precipitate, turning to grey. Solution of 'A' turns yellow coloured solution of FeCl<sub>3</sub> to a green coloured solution. Solution of 'A' gives white precipitate with NaOH, which dissolves in excess of NaOH. Moreover, the solution of 'A' gives yellow precipitate, when H<sub>2</sub>S gas is passed through it. This precipitate dissolves in yellow ammonium sulphide. Compound 'A' is found to give chromyl chloride test. Identify the compound 'A' and give the reactions involved.

Ans. Compound 'A' is 
$$SnCl_2$$
.

 $SnCl_2 + 2HgCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$ 
White

 $SnCl_2 + Hg_2Cl_2 \longrightarrow 2Hg + SnCl_4$ 
 $Grey$ 
 $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$ 
 $Green$ 
 $SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$ 
 $(White precipitate)$ 
 $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$ 
 $Soluble$ 
 $SnCl_2 + H_2S \longrightarrow 2HCl + SnS$ 
 $Yellow$ 
 $SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_3$  ]
 $Yellow$ 
 $SnS + (NH_4)_2S_3 \longrightarrow Soluble$ 
 $SnCl_2 + M_2S \longrightarrow Soluble$ 
 $SnS + (NH_4)_2S_3 \longrightarrow Soluble$ 
 $SnS + (NH_4)_2S_3 \longrightarrow Soluble$ 

9. 
$$[A] \xrightarrow{\text{HNO}_3} [B] + [C] \xrightarrow{\text{KI or } \text{K}_2\text{CrO}_4} \text{Yellow precipitate}$$

Scarlet Black Colourless solution residue  $H_2\text{S gas}$ 

(E)  $H_2\text{S gas}$ 
(D) Black precipitate

Pink of it dissolves coloured in dil. HNO<sub>3</sub> solution

What are the compounds 'A' to 'E' in above road map problem? Give the reactions involved.

[Ans. (A) 
$$Pb_3O_4$$
; (B)  $PbO_2$ ; (C)  $Pb(NO_3)_2$ ; (D)  $PbS$ ; (E)  $HMnO_4$ ]

$$[ \textbf{Hint} : Pb_3O_4 + 4HNO_3 \longrightarrow PbO_2 + 2Pb(NO_3)_2 + 2H_2O$$

$$(A) \qquad (B) \qquad (C)$$

$$Pb(NO_3)_2 + 2KI \longrightarrow PbI_2 + 2KNO_3$$
 $Yellow$ 
precipitate

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2KNO_3$$
  
Yellow

$$Pb(NO_3)_2 + H_2S \longrightarrow PbS + 2HNO_3$$
(D) Black precipitate

$$PbO_2 + Mn^{2+} + HNO_3 \longrightarrow HMnO_4 + Pb^{2+}$$
]

10. A hydrated metallic salt (A), light green in colour, gives a white anhydrous residue (B) after being heated gradually. (B) is soluble in water and its aqueous solution reacts with NO to give a dark brown compound (C). (B) on strong heating gives a brown residue (D) and a mixture of two gases (E) and (F). The gaseous mixture, when passed through acidified permanganate, discharges the pink colour and when passed through acidified BaCl<sub>2</sub>, gives a white precipitate. Identify (A), (B), (C), (D), (E) and (F).

[Ans. (A) 
$$FeSO_4.7H_2O$$
; (B)  $FeSO_4$ ; (C)  $FeSO_4.NO$   
(D)  $Fe_2O_3$ ; (E)  $SO_2$ ; (F)  $SO_3$ ]

# Revision Exercise (Chapter 16 to 18)



	GLE CORRECT ANSWER TYPE		(a) 100L □ (b) 250L □ (c) 50 mole □ (d) 250 mole □	٦. ٢
1.	Chlorine is prepared by reacting HCl with MnO <sub>2</sub> . The	9.	50 mL of a mixture of CO and H <sub>2</sub> gave 20 mL of CO <sub>2</sub> after	
	reaction is represented by the following equation:	,	combustion in excess of air. What is the percentage of CC	
	$MnO_2 + 4HCl \longrightarrow Cl_2 + MnCl_2 + 2H_2O$		by volume in the mixture?	•
	Assuming the reaction goes to completion, what mass of		(a) 40	ב
	conc. HCl solution (36% HCl by mass) is needed to produce		(c) 50	ב
	7.0 g of Cl <sub>2</sub> ?	10.	The number of moles of KMnO <sub>4</sub> that will be needed to reac	t
	(a) 20 g		with 10 moles of sulphite ion in acidic solution is:	
	(c) 40 g		(a) 1	
2.	5.2 g of silver carbonate on being strongly heated yield a		(c) 3	]
	residue weighing:	11.	One of the following salts does not give orange-red vapour	S
	(a) $3.01  \text{g}$		when heated with potassium dichromate and conc. H <sub>2</sub> SO	4
	(c) $5.07  \text{g}$		but dissolves in NH <sub>4</sub> OH solution. The resulting solution	n
3.	A 0.5 g sample of MnO <sub>2</sub> is treated with HCl. The liberated		gives yellow precipitate with KI. Identify the original salt.	
	chlorine is passed through KI solution. 30 mL of 0.1 M		(a) $ZnCl_2$ $\Box$ (b) $AgCl$	
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> solution is required to titrate the evolved		(c) NaCl $\Box$ (d) CaCl <sub>2</sub>	J
	iodine. The percentage of MnO <sub>2</sub> sample is:	12.	A solid liberates a brown gas on acidification and a colourles	S
	[Eq. mass of $MnO_2 = 87/2$ ]		alkaline gas on treatment with NaOH. On direct heating,	
	(a) $26.1$ $\Box$ (b) $21.6$ $\Box$		gives a colourless non-reactive gas. On complete heating	3,
	(c) 23.1		the solid completely disappears:	
4.	'A' and 'B' are two HNO <sub>3</sub> solutions having normality $0.5 N$		(a) $NaNO_2$ $\square$ (b) $NaNO_3$	
	and 0.1 N respectively. The volumes of solution 'A' and 'B'		(c) $NH_4NO_2$ $\Box$ (d) $NH_4NO_3$	
	required to make 2L solution of 0.2 N HNO <sub>3</sub> are:	13.	A salt is treated with dilute sulphuric acid to generat	e
	(a) $0.5 \text{ L}$ of A and $1.5 \text{ L}$ of B		colourless gaseous mixture which turns lime water milky an	d
	(b) $1.5 \text{ L of } A \text{ and } 0.5 \text{ L of } B$		burns with a blue flame. The salt has the acidic radical:	
	(c) $1.0 \text{ L of } A \text{ and } 1.0 \text{ L of } B$		(a) $CO_3^{2-}$	그,
	(d) $0.75 \text{ L of } A \text{ and } 1.25 \text{ L of } B$		(5) 52-35 - 5	
5.	A mixture of cuprous oxide and cupric oxide was found to	14.	The following reactions are given by a compound 'A'.	
	contain 88% copper. What is the amount of cuprous oxide		dil. HCl	
	and cupric oxide in 5 g of the sample of the mixture		Clear solution  dil. H250  K2CrO4 in acetic acid  Yellow ppt.	
	respectively: [Atomic mass of copper = 64]		dil. Habe	
	(a) $Cu_2O = 0.5 g$ ; $CuO = 4.5 g$		K <sub>2</sub> CrO <sub>4</sub> in acetic acid	
	(b) $Cu_2O = 4.0 \text{ g}$ ; $CuO = 1.0 \text{ g}$		arbite PP	
	(c) $Cu_2O = 1.0 g$ ; $CuO = 4.0 g$	•	Yellow ppt.	
٠.	(d) $Cu_2O = 4.5 \text{ g}$ ; $CuO = 0.5 \text{ g}$			•
6.	4.9 g of H <sub>2</sub> SO <sub>4</sub> is present in 100 mL of the solution. What is		The compound 'A' is:	
-	the molarity and normality of the solution?		. •	
	(a) $1 M, 1 N$		, , , , , , , , , , , , , , , , , , , ,	
_	(c) $1 M, 0.5 N$	15.	From the following information, identify $(A)$ and $(B)$ :	
7.	0.1435 g of AgCl is obtained from 20 mL HCl. What is the		$(A) + H_2SO_4 \longrightarrow (B)$	
	normality of the acid?		a colourless irritating ga	ìS
	(a) $0.5 N$ $\square$ (b) $0.1 N$ $\square$		$(B) + K_2Cr_2O_7 + H_2SO_4 \longrightarrow Green soln.$	
_	(c) $0.05N$		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	
8.	Assuming that petrol is isooctane ( $C_8H_{18}$ ) and has a density			
	0.8 g mL <sup>-1</sup> . 2.85 L petrol on complete combustion will	16.	Cu <sup>2+</sup> and Cd <sup>2+</sup> are detected in a mixture of their solutions b	y

using:

consume how much of oxygen gas at NTP?

 $As_2S_3$  is soluble.

	(a) KCN, $H_2S$ $\square$ (b) HCl, $H_2S$ $\square$ (c) $K_4Fe(CN)_6$ , $H_2S$ $\square$ (d) Conc. HNO <sub>3</sub> , $H_2S$ $\square$	(a) 35.5
17.	When $H_2S$ is passed through $Hg_2^{2+}$ , the precipitate formed	
	consists of:	ONE OR MORE THAN ONE CORRECT ANSWERS TYPE
	(a) $Hg_2S$ $\Box$ (b) $HgS$ $\Box$	•
10	(c) $HgS + Hg_2S$ $\Box$ (d) $HgS + Hg$ $\Box$	25. Which of the following is/are primary standard?
18.	A mixture of Bi(OH) <sub>3</sub> , Zn(OH) <sub>2</sub> , Pb(OH) <sub>2</sub> and Al(OH) <sub>3</sub> is	(a) $KMnO_4$ $\Box$ (b) $KOH$ $\Box$
	dissolved in excess of sodium hydroxide. The insoluble portion is then dissolved in HCl. One part of the solution	(c) $Na_2CO_3 \cdot 10H_2O$ $\Box$ (d) $H_2C_2O_4 \cdot 2H_2O$ $\Box$
	when reacted with sodium stannite gives black precipitate.	<ul><li>26. Identify the incorrect statement/s.</li><li>(a) The equivalent mass of KMnO<sub>4</sub> in alkaline medium is one</li></ul>
	The other part when diluted with large volume of water must	third of its molecular mass.
	give:	(b) The mass of oxalic acid dihydrate required to prepare
	(a) white turbidity $\Box$ (b) green precipitate $\Box$	500 mL of 0.02 N solution is 6.3 g. $\Box$
	(c) blue colouration $\square$ (d) red vapour $\square$	(c) The volume of 0.1 $M$ K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solution required to
19.	The third group of qualitative analysis, the reagent mixture	oxidise 35 mL of 0.5 M FeSO <sub>4</sub> solution in acidic medium
	of NH <sub>4</sub> Cl and NH <sub>4</sub> OH is employed. If NH <sub>4</sub> Cl is not available	is 29.17 mL. □
	and the mixture does not contain Mn <sup>2+</sup> , which of the	(d) Phenolphthalein can be used as an indicator in iodometry.
	following can be used?	
	(a) $(NH_4)_2SO_4$ $\Box$ (b) $(NH_4)_2CO_3$ $\Box$	27. Which of the following metal ions form yellow precipitate
20	(c) $NH_4NO_3$	with K <sub>2</sub> CrO <sub>4</sub> solution?
20.	In acidic medium, KMnO <sub>4</sub> oxidises FeSO <sub>4</sub> solution. Which	(a) $Fe^{2+}$
	of the following statements is correct?  (a) 10 mL of 1 N KMnO <sub>4</sub> solution oxidises 10 mL of	(c) $Pb^{2+}$ $\Box$ (d) $Ba^{2+}$ $\Box$
	$5 N \text{ FeSO}_4$ solution	28. Heating with concentrated HNO <sub>3</sub> and an ammonium molybdate solution, a salt solution gives a yellow precipitate.
	(b) 10 mL of 1 $M$ KMnO <sub>4</sub> solution oxidises 10 mL of 5 $M$	It may be:
	KMnO <sub>4</sub> solution □	(a) $As_2S_3$ $\Box$ (b) $CuSO_4$ $\Box$
	(c) 10 mL of 1 M KMnO <sub>4</sub> solution oxidises 10 mL of 1 M	(c) $Na_3PO_4$ $\square$ (d) $BaCl_2$ $\square$
	FeSO <sub>4</sub> solution □	29. Which of the following reagents will be useful in separating
	(d) 10 mL of 1 N KMnO <sub>4</sub> solution oxidises 10 mL of 0.1 N	a mixture of Zn <sup>2+</sup> and Cu <sup>2+</sup> ions?
۵,	FeSO <sub>4</sub> solution	(a) $H_2S$ in alkaline medium
21.	When a pinch of a salt is added to dilute acid, it evolves a	(b) $H_2S$ in acid medium
	gas that turns acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> green. The sulphide precipitate in fourth group is dissolved in aquaregia. The	(c) Excess NaOH solution
	solution when shaken with sodium bicarbonate and bromine	<ul> <li>(d) Na<sub>2</sub>S in neutral medium</li> <li>30. Potassium iodide is added to freshly precipitated mercury (II)</li> </ul>
	water develops apple green colour. The basic and acidic	iodide. Which is/are the correct statement/s?
	radicals of the salt are:	(a) The precipitate will dissolve
	(a) $Ni^{2+}$ , $SO_3^{2-}$ $\Box$ (b) $Co^{2+}$ , $SO_3^{2-}$ $\Box$	(b) The solution possesses the anion $[HgI_4]^{2-}$
	(c) $Ni^{2+}$ , $S^{2-}$	(c) The solution can be used for the test of ammonium ion
22.	What mass of hydrated oxalic acid should be added for	
	complete neutralisation of 100 mL of 0.2 N NaOH?	(d) All the above statements are wrong $\Box$
	(a) 0.90 g	ACCEPTION DEACON TYPE OUECTIONS
22	(c) 1.08 g	ASSERTION-REASON TYPE QUESTIONS
23.	Haemoglobin contains 0.33% iron by mass. If the molecular mass of haemoglobin is 68000, how many iron atoms are	Each of the following questions contains Assertion (A) and
	present in each molecule of haemoglobin?	<b>Reason (R).</b> Use the following key to select one appropriate answer.  (a) If both (A) and (R) are true and (R) is a correct
	(a) 1	explanation for (A).
	(c) 3	(b) If both (A) and (R) are true and (R) is not a correct
24.	5.0 g of bleaching powder was suspended in water and	explanation for (A).
	volume made up to half a litre. 20 mL of this suspension when	(c) If (A) is true and (R) is false.
	acidified with acetic acid and treated with excess of KI	(d) If (A) is false and (R) is true.
	solution liberated iodine which required 20 mL of a	31. (A) CdS and As <sub>2</sub> S <sub>3</sub> both are yellow coloured precipitates.
	decinormal hypo solution for titration. What is the percentage	(R) CdS is insoluble in yellow ammonium sulphide while

of available chlorine in bleaching powder.

- 32. (A) All sulphates give white precipitate with BaCl<sub>2</sub> solution.
  - (R) BaSO₄ is insoluble in water.
- 33. (A) Borax bead test is used to detect the cations like Cu<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup> and Co<sup>2+</sup>.
  - (R) The cations like Cu<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, etc., form coloured metaborates.
- 34. (A) Dimethyl glyoxime is used for the test of Ni<sup>2+</sup> ion.
  - (R) Dimethyl glyoxime forms a complex with Ni<sup>2+</sup> ion. The complex has a dark blue colour.
- **35.** (A) The molecular mass of  $H_3PO_3$  is 82. Its equivalent mass is 41.
  - (R) H<sub>3</sub>PO<sub>3</sub> is a dibasic acid.
- **36.** (A) A normal solution contains one gram equivalent mass of the substance in 1000 grams of the solvent.
  - (R) A solution which has been prepared from pure substance is termed standard solution.
- 37. (A) Mole fraction and molality are independent of temperature.
  - (R) Normality and molarity are dependent on temperature.
- 38. (A) Starch is the indicator used in the iodometric titrations.
  - (R) In the titration of ferrous ammonium sulphate against potassium dichromate, K<sub>4</sub>Fe(CN)<sub>6</sub> solution is used as external indicator.

Column-II

(s) Chocolate ppt, test of Cu<sup>2+</sup>

#### MATRIX MATCHING QUESTIONS

39. Match the following:

#### (Sulphides) (Colour/group) (a) HgS (p) Black (b) NiS (q) Dirty white (c) SnS (r) Basic radical IInd group (d) ZnS (s) Basic radical IVth group 40. Match Column-II: Column-I Column-II (Reagents) (Uses) (a) $K_2Cr_2O_7$ (p) Chromyl chloride test (g) Prussian blue test of Fe<sup>3+</sup> (b) K<sub>4</sub>Fe(CN)<sub>6</sub> (c) NaOH (r) Test of sulphite

41. Match Column-I with Column-II:

(d) Pb(CH<sub>3</sub>COO)<sub>2</sub>

Match Column-I with Column-II:				
Column-I		Column-II		
(Reaction)		(Equivalent mass)		
(a) $K_2Cr_2O_7 \longrightarrow Cr_2(SO_4)_3$	(p)	Oxidising agent		
(b) $KMnO_4 \longrightarrow K_2MnO_4$	(q)	Mol. mass		
(c) $2Na_2S_2O_3 + I_2$	(r)	$\frac{\text{Mol. mass}}{6}$		
$\longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$ (d) $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{O}$	(s)	Reducing agent		
$\longrightarrow$ Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + H <sub>2</sub> O				

(t) NH<sub>4</sub> ion

#### INTEGER ANSWER TYPE

- **42.** 13.4 g of a sample of a salt  $Na_2SO_4 \cdot xH_2O$  was found to contain 6.3 g of water. What is the value of x?
- **43.** 17 g of pure H<sub>2</sub>O<sub>2</sub> is decomposed. The mass of oxygen evolved is:
- 44. A mixture of marsh gas (CH<sub>4</sub>) and acetylene requires 22 mL of oxygen for complete combustion and produces 14 mL of CO<sub>2</sub>. What is the volume of marsh gas in the mixture?
- **45.** 4 moles of H<sub>2</sub>S and 22.4 L of SO<sub>2</sub> at STP react according to following equation,

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$$

What will be the number of moles of sulphur formed in the reaction?

- **46.** 4.9 g of H<sub>2</sub>SO<sub>4</sub> is present in 100 mL of the solution. What is the normality of the solution?
- 47. 0.175 g of a metal was dissolved in 50 mL N-acid. The whole solution required 20.85 mL of normal alkaline solution to neutralise the excess of acid. What is the equivalent mass of the metal?
- 48. What is the mass in grams of available O<sub>2</sub> per litre from a solution of H<sub>2</sub>O<sub>2</sub>, 5 mL of which when titrated with N/20 KMnO<sub>4</sub> solution required 25 mL for the reaction.

  2KMnO<sub>4</sub> + 5H<sub>2</sub>O<sub>2</sub> + 4H<sub>2</sub>SO<sub>4</sub> → 5O<sub>2</sub> + 8H<sub>2</sub>O

+ 2KHSO<sub>4</sub> + 2MnSO<sub>4</sub>

#### LINKED COMPREHENSION TYPE

#### Passage 1

Compound 'A' reduces  $HgCl_2$  to a white precipitate, turning to grey. Solution of 'A' gives white precipitate with NaOH, which dissolves in excess of NaOH. The solution of 'A' in dilute HCl gives yellow precipitate on passing  $H_2S$ . Compound 'A' mixed with  $K_2Cr_2O_7$  and heated with conc.  $H_2SO_4$  gives vapours which when passed through NaOH solution form yellow coloured solution.

- **49.** Compound 'A' is:
  - (a) CdCl<sub>2</sub>

(b) PbCl<sub>2</sub>

(c) SnCl<sub>2</sub>

- (d) BiCl<sub>3</sub>
- **50.** The precipitate formed by NaOH with solution of 'A' is:
  - (a) Sn(OH)Cl
- (b)  $Sn(OH)_2$

(c) SnO

- (d) SnO<sub>2</sub>
- **51.** The vapours evolved when compound 'A' is heated with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and conc. H<sub>2</sub>SO<sub>4</sub> are:
  - (a) chlorine
- (b) chlorine dioxide
- (c) hydrogen chloride
- (d) chromyl chloride
- **52.** Compound 'A' gives white ppt. with HgCl<sub>2</sub>. The name of white compound is:
  - (a) Calomel
- (b) Corrosive sublimate
- (c) Vermilon
- (d) Millon's base

#### Passage 2

Compound 'A' is a light green solid. It gives the following tests.

- (a) It dissolves in dilute H<sub>2</sub>SO<sub>4</sub>. No gas is evolved.
- (b) Compound 'A' is heated strongly. Two gases (B) and (C) with pungent smell come out and brown residue (D) is left.
- The gaseous mixture is passed into acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution, it turns green.
- (d) The residue 'D' from reaction (b) on boiling with HCl acid gives a vellow solution 'E'. The vellow solution on treatment with ammonium thiocyanate gives a blood red solution.
- **53.** Compound 'A' shows reducing properties.
  - (a) FeSO<sub>4</sub>
- (b) NiSO<sub>4</sub>
- (c)  $Cr_2(SO_4)_3$
- (d)  $Fe_2(SO_4)_3$
- 54. The residue 'D' is:
  - (a) Cr<sub>2</sub>O<sub>3</sub>

(b) NiO

- (c)  $Fe_2O_3$
- (d) FeO
- **55.** The solution 'E' contains:
  - (a) FeCl<sub>2</sub>

(b) FeCl<sub>3</sub>

(c) CrCl<sub>3</sub>

(d) NiClo

# fuswers with Hints

1. (c) 
$$MnO_2 + 4HCl \longrightarrow Cl_2 + MnCl_2 + 2H_2O$$
  
 $4 \times 36.5 \text{ g}$  71 g

HCl needed for 7 g Cl<sub>2</sub> = 
$$\frac{4 \times 36.5}{71} \times 7 = 14.39$$
 g

36% HCl soln. required = 
$$\frac{100}{36} \times 14.39 \approx 40$$

$$Ag_2CO_3 \longrightarrow 2Ag + CO_2 + \frac{1}{2}O_2$$
276 g, 216 g

Residue obtained from 5.2 g Ag<sub>2</sub>CO<sub>3</sub> =  $\frac{216}{276} \times 5.2 = 4.07$ 

3. (a) 30 mL 0.1 
$$M$$
 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 30 mL 0.1  $N$  Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>  
= 30 mL 0.1  $N$  Cl<sub>2</sub>  
= 30 mL 0.1  $N$  MnO<sub>2</sub>

Amount of MnO<sub>2</sub> = 
$$\frac{87}{2} \times \frac{0.1}{1000} \times 30 = 0.1305$$
 g

% of MnO<sub>2</sub> = 
$$\frac{0.1305}{0.5} \times 100 = 26.1$$

4. (a) Let xL of A be mixed with (2-x) L of B.

$$x \times (0.5) + (2 - x) \times (0.1) = 2 \times (0.2)$$

$$x = \frac{0.2}{0.4} = 0.5$$

5. (d) 
$$Cu_2O \longrightarrow 2Cu$$

$$144 g = 2 \times 6$$

$$= 128$$

$$CuO \longrightarrow Cu$$

Let 'a' g  $Cu_2O$  and (100 - a)g CuO be present in 100 g of the mixture.

$$\frac{128}{144} \times a + \frac{64}{80} \times (100 - a) = 88$$

$$a = 90$$

#### Passage 3

1.325 g of anhydrous sodium carbonate are dissolved in water and the solution made upto 250 mL. On titration, 25 mL of this solution neutralise 20 mL of sulphuric acid.

- 56. Normality of Na<sub>2</sub>CO<sub>3</sub> solution is:
  - (a) 1 N

(b) 0.1 N

(c) 0.5 N

- (d) 0.01 N
- 57. Normality of the sulphuric acid solution is:
  - (a) 1/2

(b) 1/4

(c) 1/8

- (d) 1/16
- 58. How much water be added to 450 mL of the H<sub>2</sub>SO<sub>4</sub> solution to make it exactly N/12?

 $Cu_2O = \frac{90}{100} \times 5 = 4.5 g$ 

Strength of the soln.  $=\frac{4.9}{100} \times 1000 = 49$ 

7. (c) No. of g equivalents of AgCl obtained =  $\frac{0.1435}{1435} = 0.001$ 

Number of moles of isooctane =  $\frac{2280}{114}$  = 20

(d) Mass of petrol =  $2850 \times 0.8 = 2280$  g

 $CuO = \frac{10}{100} \times 5 = 0.5 \text{ g}$ 

Molarity =  $\frac{\text{Strength}}{\text{Mol. mass}} = \frac{49}{98} = 0.5$ 

Thus, 20 mL of HCl contains 0.001 g equivalents of HCl.

Normality =  $\frac{0.001}{20} \times 1000 = 0.05 N$ 

 $C_8H_{18} + \frac{25}{2}O_2 \longrightarrow 8CO_2 + 9H_2O$ 1 mole 25/2 mole 25/2 mole

Normality =  $2 \times Molarity = 2 \times 0.5 = 1.0$ 

- (a) 225 mL
- (b) 125 mL
- (c) 175 mL
- (d) 200 mL

- 2. (b) Ag<sub>2</sub>CO<sub>3</sub> on strong heating gives silver metal.

$$Ag_2CO_3 \longrightarrow 2Ag + CO_2 + \frac{1}{2}O$$
276 g. 216 g

Amount of MnO<sub>2</sub> = 
$$\frac{87}{2} \times \frac{0.1}{1000} \times 30 = 0.1305 \text{ g}$$

$$x = \frac{0.2}{0.1} = 0.5$$

(a)  $\underset{1 \text{ vol}}{\text{CO}} + \frac{1}{2} \text{O}_2 \longrightarrow \underset{1 \text{ vol}}{\text{CO}_2}$ 

$$\% = \frac{20}{50} \times 100 = 40$$

- 11. (b) AgCl—It is a covalent chloride. It dissolves in ammonium hydroxide and forms a complex which is soluble.

$$AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O$$
Soluble

It combines with KI and forms yellow precipitate of AgI.

$$Ag(NH_3)_2Cl + KI \longrightarrow AgI + 2NH_3 + KCl$$

12. (c)  $NH_4NO_2$   $2NH_4NO_2 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + NO_2 + NO_2 + H_2O$   $NH_4NO_2 + NaOH \longrightarrow NH_3 + NaNO_2 + H_2O$  $NH_4NO_2 \xrightarrow{\text{Heat}} N_2 + 2H_2O$ 

- 13. (d) Oxalate—It gives out mixture of two gases CO<sub>2</sub> and CO. CO<sub>2</sub> turns lime water milky and CO burns with blue flame.
- 14. (c) BaCO<sub>3</sub>

$$BaCO_3 + 2HCl \longrightarrow BaCl_2 + CO_2 + H_2O$$
Clear
Soln.

 $BaCO_3 + H_2SO_4 \longrightarrow BaSO_4 + H_2O + CO_2$ White ppt.

$$BaCO_3 + 2CH_3COOH + K_2CrO_4 \longrightarrow$$
  
 $BaCrO_4 + 2CH_3COO$ 

 $\begin{array}{l} \text{BaCrO}_4 + 2\text{CH}_3\text{COOK} + \text{CO}_2 + \text{H}_2\text{O} \\ \text{Yellow ppt.} \end{array}$ 

15. (d) Sulphite 
$$+ H_2SO_4 \longrightarrow SO_2$$

$$(A) \qquad (B) \qquad (B)$$
 $3SO_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$ 
Green Solph

- 16. (a) KCN forms cyanide complexes with copper and cadmium salts. The cadmium complex is not stable and combines with H<sub>2</sub>S to form yellow ppt., CdS.
- 17. (d)  $Hg_2^{2+} + H_2S \longrightarrow HgS + Hg + 2H^+$
- (a) Bi(OH)<sub>3</sub> does not dissolve in NaOH. It dissolves in HCl.

$$Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O$$

$$2BiCl_3 + 3Na_2SnO_2 + 6NaOH \longrightarrow 3Na_2SnO_3 + 2Bi + 6NaCl + 3H_2O$$

$$BiCl_3 + H_2O \longrightarrow BiOC1 + 2HC1$$
White

- 19. (c) (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> cannot be used as it will give white ppt. of barium and strontium sulphates. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> will give white ppt. if Ba<sup>2+</sup>, Sr<sup>2+</sup> and Ca<sup>2+</sup> ions are present. To suppress the ionisation of NH<sub>4</sub>OH, NH<sub>4</sub>NO<sub>3</sub> can be used if Mn<sup>2+</sup> ion is not present.
- 20. (b) 2KMnO<sub>4</sub>+8H<sub>2</sub>SO<sub>4</sub>+10FeSO<sub>4</sub>——
  2 mole 10 mole 5 mole

$$K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

- 21. (b) The gas SO<sub>2</sub> turns K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> soln. green. The acidic radical present is SO<sub>3</sub><sup>2</sup>.
   Under the conditions, K<sub>3</sub>[Co(CO<sub>3</sub>)<sub>3</sub>] is formed which is apple green in colour. Thus, the salt consists Co<sup>2+</sup> as cation.
- 22. (d) 100 mL 0.2 N NaOH = 100 mL 0.2 N oxalic acid Amount of oxalic acid =  $\frac{63 \times 0.2 \times 100}{1000}$  = 1.26 g
- 23. (d) Amount of iron present in molecular mass of haemoglobin

$$=\frac{0.33}{100} \times 68000 = 0.33 \times 680 \text{ g}$$

Number of iron atoms = 
$$\frac{0.33 \times 680}{56} \approx 4$$

24. (a) 20 mL 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = 20 mL 0.1 N I<sub>2</sub> = 20 mL 0.1 N Cl<sub>2</sub>

Amount of chlorine = 
$$\frac{35.5 \times 0.1 \times 20}{1000} = 0.071 \text{ g}$$

Amount of chlorine in 500 mL suspension =  $\frac{0.071}{20} \times 500 = 1.775$ 

% available chlorine = 
$$\frac{1.775}{5} \times 100 = 35.5$$

- 25. (c, d)
- **26.** (a, d)
  - (a) The equivalent mass of KMnO<sub>4</sub> in alkaline medium

= Mol, mass

(b) Mass of oxalic acid = 
$$\frac{63 \times 0.02 \times 500}{1000} = 6.3 \text{ g}$$

(c) 
$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3$$
  
1 mole 6 mole + 3Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 7H<sub>2</sub>O  
0.1 × V = 1/6 [35.0 × 0.5]

$$0.1 \times V = 1/6 [35.0 \times 0.5]$$
  
  $V = 29.17$ 

- (d) Phenolphthalein is used as indicator in acid-base titrations.
- 27. (c, d) 28. (a, c) 29. (a, b, c) 30. (a, b, c) 31. (b)
- 32. (a) 33. (a) 34. (c) 35. (a) 36. (d)
- 37. (b) 38. (c)
- **39.** (a-p, r); (b-p, s); (c-r); (d-q, s)
- **40.** (a-p, r); (b-q, s); (c-p, t); (d-p)
- 41. (a-p, r); (b-p, q); (c-q, s); (d-q, s)
- 42. (7) Mol. mass of Na<sub>2</sub>SO<sub>4</sub> xH<sub>2</sub>O = 2 × 23 + 32 + 4 × 16 + x × 18 = (142 + 18x)

or 
$$\frac{6.3}{13.4} \times (142 + 18x) = 18x$$

$$6.3 \times (142 + 18x) = 13.4 \times 18x$$

$$142 \times 6.3 = 13.4 \times 18x - 6.3 \times 18x$$

$$= 18x (13.4 - 6.3) = 18x \times 7.1$$

$$x = \frac{142 \times 6.3}{18 \times 7.1} = 7$$

43. (8) 
$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
68 g  $32$  g
$$32 = 32$$

Mass of O<sub>2</sub> evolved = 
$$\frac{32}{68} \times 17 = 8$$
 g

On solving both the equations, we get

$$a = 6 \text{ mL}, b = 4 \text{ mL}$$

1 mole of SO<sub>2</sub> will react with 2 moles of H<sub>2</sub>S and will form 3 moles of S.

**46.** (1) Strength of 
$$H_2SO_4 = \frac{4.9}{100} \times 1000 = 49 \text{ g/L}$$

Normality = 
$$\frac{\text{Strength}}{\text{Eq. mass}} = \frac{49}{49} = 1$$

47. (6) 20.85 mL *N*-alkaline soln. = 20.85 N-acid soln.

The acid utilised for dissolving the metal

Thus, 
$$0.175 = \frac{x \times 1 \times 29.15}{1000}$$
 (x = Eq. mass of metal)  
$$x = \frac{175}{29.15} \approx 6$$

**48.** (2) Normality of H<sub>2</sub>O<sub>2</sub> soln. 
$$=\frac{25}{20} \times \frac{1}{5} = \frac{1}{4}$$

Strength of 
$$H_2O_2$$
 soln.  $=\frac{1}{4} \times 17 = \frac{17}{4}$   
 $2H_2O_2 \longrightarrow 2H_2O + O_2$   
68 g 32 g

Available oxygen = 
$$\frac{32}{68} \times \frac{17}{4} = 2 \text{ g}$$

**49.** (c) The compound gives chromyl chloride. It is a reducing agent and gives yellow ppt. with H<sub>2</sub>S. Hence, it is SnCl<sub>2</sub>.

50. (b) 
$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$$
  
 $Sn(OH)_2$  dissolves in excess of NaOH.  
 $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$ 

51. (d) 
$$2\text{SnCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + 3\text{H}_2\text{SO}_4 \longrightarrow \\ 2\text{CrO}_2\text{Cl}_2 + \text{K}_2\text{SO}_4 + 2\text{SnSO}_4 + 3\text{H}_2\text{O}_4 - \\ \text{changed}$$

chloride

2. (a) 
$$Hg_2Cl_2$$
 is called calomel.  
 $SnCl_2 + 2HgCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$ 

53. (a) 
$$2\text{FeSO}_4 \xrightarrow{\text{Heat}} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$$

$$(A) \qquad (D) \qquad (B) \qquad (C)$$

$$\text{turns } K_2\text{Cr}_2\text{O}_7$$

$$\text{soln. green}$$

55. (b) 
$$Fe_2O_3 + 6HCl \longrightarrow FeCl_3 + 3H_2O$$

Yellow solution

**56.** (b) Eq. mass of 
$$Na_2CO_3 = \frac{106}{2} = 53$$

Normality of Na<sub>2</sub>CO<sub>3</sub> soln. = 
$$\frac{4 \times 1.325}{53} = \frac{1}{10}N$$

57. (c) Normality of H<sub>2</sub>SO<sub>4</sub> soln. = 
$$25 \times \frac{1}{10} \times \frac{1}{20} = \frac{1}{8}N$$

$$N_B V_B = N_A V_A$$
(Before (After dilution) dilution)
$$\frac{1}{8} \times 450 = V_A \times \frac{1}{12}$$

$$V_A = \frac{450}{8} \times 12 = 675 \text{ mL}$$

Water to be added = (675 - 450) = 225 mL

# CHAPTER 19

# **Environmental Chemistry**

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### 19.1

#### INTRODUCTION

The earth, where various forms of life live and survive under different conditions, is a unique planet of the solar system. This is perhaps partly due to optimum distance of the earth from the sun. The temperature of the earth is neither too hot as in Venus and Mercury nor it is too cold as in Jupiter and other planets. The envelope of air surrounding the earth contains gases and provides oxygen which is essential for survival of most forms of life. The air envelope also regulates the temperature on earth's surface. The moderate temperature conditions also help in the regulation of water in different forms in the atmosphere, as well as on the earth. Thus, earth is a unique planet which has been gifted by nature, a life supporting region known as a biosphere (the environment which supports life and sustains various human activities; it extends to about 20 km from the bottom of the ocean to the highest point in the atmosphere at which life can survive). Various forms of life in the biosphere exist as microbes, plants and animals. These forms of life living in a particular region of biosphere depend on the physical and chemical non-living as well as living components of environment. The non-living components of the environment comprise the atmosphere (air), hydrosphere (water) and lithosphere (land) whereas the living or biological component is biosphere, which includes plants, animals and other organisms. The environment or surroundings of an organism, therefore, includes (i) atmosphere (ii) hydrosphere (iii) lithosphere

and (iv) biosphere. Man on this planet occupies a central position and makes use of other forms of life in the biosphere for various purposes such as food, shelter, etc. It is, thus, essential to study the various components of environment that affect the man and other forms of life on this planet.

Environmental chemistry is defined as the study of chemical phenomenon in the environment or refers to the study of sources, reactions, transport, effects and fates of various chemical species in the air, water and soil environment. Environmental chemistry is not a single disciplinary science but a multidisciplinary science which covers many vastly different fields such as chemistry, physics, biological sciences, agriculture, medical science, public health, sanitary engineering, etc.

The term environmental chemistry has come to be regarded as synonymous with environmental pollution by some scientists. While sticking to this narrow definition, they highlight only the problem of pollution resulting from the varied uses of chemicals yet it must be emphasised that environmental chemistry deals with a wider aspect of knowledge. The problem of pollution is just a small segment of environmental chemistry. The application of energy resources no doubt provided comfort and happiness to man, but it also started degrading his habitat. It soon became apparent that contamination of natural environment threatened

the very existence of mankind, *i.e.*, environmental pollution is becoming a matter of concern for one and all today. A need of conservation of environment is being raised at all national and international levels. Thus, the awareness about various aspects of environment becomes very important for every human being today.

#### 19.2 COMPONENTS OF ENVIRONMENT

#### 1. ATMOSPHERE

It is a protective blanket of gases which is surrounding the earth. The atmosphere extends to thousands of kilometre above the earth's surface. It has no well defined upper limits and gradually merges with the outer space. The atmosphere is held to the earth by the force of gravity. Of the total mass of atmosphere, about 99% is within a height of 30 km from the earth's surface. The total mass of the atmosphere is about  $5 \times 10^{15}$  metric tonnes.

Composition: The constituents which make up the atmosphere are gases, water vapours and aerosols. With increasing height above sea level, the atmospheric pressure gradually decreases. The atmosphere consists relatively uniform composition in the lower layers near the earth if water vapours and aerosols are excluded. The major gases in the air are nitrogen and oxygen. Pure dry air, on an average, constitutes 78% nitrogen and 21% oxygen by volume. Remaining 1% accounts for other gases.

Major components :  $N_2$ ,  $O_2$ , water vapours

Minor components: Ar, CO<sub>2</sub>

Tracer components: He, Ne, Kr, Xe, CH<sub>4</sub>, H<sub>2</sub>, CO, N<sub>2</sub>O, NO, NO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub>, O<sub>3</sub>, HCHO, etc.

The composition of dry atmosphere by volume is given in the following table:

Gas	Per cent	Gas	Per cent
Nitrogen,	78.08	Methane	0.00015
Oxygen	20.95	Nitrous oxide	0.000025
Argon	0.93	Hydrogen	0.00005
Carbon dioxide	0.033	Ozone	0.000004
Neon	0.0018	Xenon	0.000008
Helium	0.00052	Sulphur dioxide,	1
Krypton	0.00011	nitrogen dioxide,	Minute quantities
		ammonia, carbon	
		monoxide, iodine, etc.	

The main constituents of the atmosphere which are responsible for sustaining life on earth are nitrogen, oxygen and carbon dioxide along with water vapour. The constituents which are of great importance for earth's climatic conditions are water vapour dust particles, carbon dioxide and ozone.

Structure or Regions of the Atmosphere: The atmosphere is divided into four major regions depending on the height as shown below:

Region	Height range (km)	Temperature range (°C)	Main constituents
Troposphere	0–11	15 to -56	O <sub>2</sub> , N <sub>2</sub> , H <sub>2</sub> O, CO <sub>2</sub>
Stratosphere	11–50	−56 to −2	O <sub>3</sub>
Mesosphere	50–90	-2 to -92	O <sub>2</sub> <sup>+</sup> , NO <sup>+</sup>
Thermosphere	90–500	-92 to 1200	$O_2^+, O^+, NO^+, N^+$

- (i) Troposphere: It is the lowest region of the atmosphere, *i.e.*, closest to earth's surface. It extends roughly to a height of about 11 km. This is the region of all living organisms including animals and plants. About 70% of the total mass of the atmosphere and practically all the water vapours and dust particles are concentrated in this region. All the dramatic events of weather (rain, lightning, hurricane, etc.), occur in this region. The temperature in this region steadily decreases from ground temperature of about 15°C to about -56°C. The minimum temperature is at about 11 km above earth's surface. This point is called **tropopause.** It contains mainly nitrogen and oxygen. It also contains argon, carbon dioxide, water vapours, aerosols and traces of many other gases. The composition of air in this region remains more or less constant provided there is no significant air pollution.
- (ii) Stratosphere: The next region is stratosphere which extends from 11 km to 50 km. The temperature in this region rises from -56°C to -2°C. This increase is due to absorption of solar radiation. This region is rich in ozone which absorbs harmful UV radiations of the sun and converts them into heat. In this way ultraviolet radiations are prevented to reach the earth. Ozone is formed from oxygen by a photochemical reaction. The ozone content of the stratosphere is more or less constant. Besides ozone, stratosphere also contains nitrogen, oxygen and small amount of water vapours. This region is free from turbulent conditions or changing weather pattern.
- (iii) Mesosphere: Next to stratosphere is the mesosphere which extends upto the height of 90 km. The lowest temperature of -92°C is observed in this region. This is due to low concentrations of ozone, oxygen and nitrogen present and thus possesses little capacity to absorb solar radiation.
- (iv) Thermosphere: This is the region above mesosphere and extends upto the height of 500 km. The temperature in this region rises from −92°C to 1200°C. This is due to the bombardment of molecular oxygen and nitrogen and atomic species by energetic particles, such as electrons and protons, from the sun. Thus, this is an electrically charged zone. Typical reactions in this zone are:

$$N_2 \longrightarrow 2N$$
  $\Delta H^\circ = 941.4 \text{ kJ}$   
 $N \longrightarrow N^+ + e^ \Delta H^\circ = 1400 \text{ kJ}$   
 $O_2 \longrightarrow O_2^+ + e^ \Delta H^\circ = 1176 \text{ kJ}$ 

The reverse of these processes liberates an equivalent amount of energy, mostly as heat. The temperature becomes about 1000°C near 400 km height. The ionised particles are responsible for the reflection of radiowaves on earth and enable wireless communication.

[The region between the altitudes of 50 km and 100 km is called **ionosphere**. In this region, there are high concentrations of ions like  $O_2^+$ ,  $O_2^+$ ,  $O_2^+$  and electrons.]

The region above the thermosphere which extends upto a height of 1600 km and merges with outerspace is called **exosphere.** It contains mainly atomic and ionic oxygen, hydrogen and helium.

# Chemical and Photochemical Reactions in Atmosphere

Many chemical and photochemical reactions are occuring in atmosphere in which main constituents such as oxygen, nitrogen, carbon dioxide, etc., are involved.

#### **Reactions Occurring in Troposphere**

The carbon dioxide and water present in atmosphere are used by green plants in the presence of sunlight to form glucose. The process is termed as photosynthesis. In this process chlorophyll (the green colouring material in plants) plays a role of a catalyst.

$$6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{hv} \text{Chlorophyll} C_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$$

The process of photosynthesis can be represented by the following equations also:

$$CO_{2} + 4H^{+} + 4e^{-} \longrightarrow C_{2} + 4H^{+} + 4e^{-}$$

$$CO_{2} + 4H^{+} + 4e^{-} \longrightarrow [CH_{2}O] + H_{2}O$$

$$\downarrow$$

$$C_{6}H_{12}O_{6}$$

Photosynthesis releases oxygen to atmosphere.

In troposphere, oxygen takes part in energy producing reactions like burning of fossil fuels.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + Energy$$
(Natural gas)

Oxygen is also utilised in the degradation of organic material by aerobic organisms.

Organic matter + 
$$O_2 \xrightarrow{\text{Aerobic} \atop \text{organisms}} CO_2 + H_2O$$

Chemical reactions such as hydrolysis, oxidation, etc., involving oxygen occur at the surface of the earth. Rusting of iron is one such example.

$$4\text{Fe} + 3\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3$$

Though nitrogen by itself is inert and unreactive, its presence in atmosphere is extremely important, since, it dilutes the harmful effects of pure oxygen (in pure oxygen most of the organic matter is burned). Electrical disturbances in the atmosphere initiates reactions between nitrogen and oxygen.

$$N_2 + O_2 \xrightarrow{h\nu} 2NO \xrightarrow{O_2} 2NO_2 + \xrightarrow{Rain} HNO_3$$

$$\xrightarrow{Alkaline}_{\substack{\text{substances} \\ \text{in soil}}} Nitrates$$

Free nitrogen is also converted into nitrates by nitrifying bacteria. This conversion is termed as nitrogen fixation. It can be represented as:

$$N_2 \xrightarrow{\text{Nitrogenase}} NH_3 \longrightarrow NO_2^- + \xrightarrow{\text{In soil}} NO_3^-$$

Nitrogen is returned to atmosphere by breaking down of nitrates in the soil in denitrification process by some soil microorganisms.

$$4NO_3^- + 2H_2O \longrightarrow 2N_2 + 5O_2 + 4OH^-$$

Some of the gaseous components of the atmosphere like water vapours, carbon dioxide, nitrous oxide and methane allow the solar radiation to pass through, but do not allow the terrestrial radiation to escape. This is what the glass does in a greenhouse. The gases absorb the heat energy reflected by earth's surface and re-emit part of it towards the surface and hence, the air near the surface becomes warmer and therefore, an increase in average temperature is observed. These gases are called greenhouse gases and the phenomenon as greenhouse effect. The concentration of these gases decreases with height, hence the greenhouse effect decreases, i.e., at this altitude the energy reflected by earth's surface is not retained by absorption and is transmitted to outer space. For this reason temperature within the troposphere decreases with increasing altitude. It drops to about -56°C by the time an altitude of 10-11 km is reached.

The concentration of the water vapours varies from place to place and from time to time at the same place. The global average of water vapours is about 1%, but it can be as high as 4%. The amount of water vapours over a given region also varies with height. About 90% of the atmospheric moisture lies below an altitude of 5 km. As the vapours are carried upwards, they cool, condense into cloud particles and return to the earth's surface by precipitation (rain or snow).

Another important constituent of troposphere is the aerosols or suspended particles. In urban and industrial areas, the concentration of aerosols may be high. These particles are mostly concentrated in the lower layers of troposphere. Suspended particles too influence the weather conditions. Most of them act as nuclei around which water vapours condense to form clouds. They also intercept and reflect insolation of sun. Dense haze and smog are also caused by the presence of suspended particles in the atmosphere.

#### **Reactions Occurring in Stratosphere**

The principal chemical species present in the stratosphere are  $N_2$ ,  $O_2$ ,  $O_3$  and some  $H_2O$ . The far ultraviolet radiation (wavelength < 190 nm) are filtered before these reach the stratosphere. Ultraviolet radiations (> 190 nm and < 340 nm) are removed in the stratosphere due to the following reactions, *i.e.*, these dangerous and harmful radiation to living species are prevented to reach earth's surface.

$$O_2 \xrightarrow{\text{UV}} O + O$$

The highly reactive O atoms combine with oxygen molecules to form ozone.

$$O + O_2 + M \longrightarrow O_3 + M$$
 (Exothermic reaction)

where M is some inert substance such as  $N_2$ . The role of M is to absorb some of the excess energy released and prevent the spontaneous decomposition of  $O_3$  molecule. The energy which is not absorbed by M is given off as heat. Ozone absorbs UV light between 200 and 300 nm.

$$O_3 \xrightarrow{UV} O + O_2$$

$$O_3 + O \longrightarrow 2O_2$$

Hence, a cycle of ozone formation and destruction exists. Thus, the stratosphere acts as a shield against UV radiations which can induce skin cancer, cause genetic mutations and destroy crops and other forms of vegetation at the earth's surface. The formation and destruction of ozone by the natural process is a dynamic equilibrium that maintains a concentration of ozone in the stratosphere. Infrared radiations to some extent are also absorbed and re-emitted by ozone. This is also responsible for temperature rise.

#### **Reactions Occurring in Upper Atmosphere**

In the upper atmosphere (*viz.*, mesosphere, thermosphere and ionosphere) ultraviolet radiations cause photochemical reactions giving rise to excited atoms, ions and electrons.

Some reactions are given below:

$$O_{2} + hv \xrightarrow{135-176 \text{ nm}} O + O$$
Oxygen atoms
$$O_{3} + hv \xrightarrow{308 \text{ nm}} O^{+}_{0xygen \text{ ion}} + O_{2} + e$$

$$O_{2} + hv \longrightarrow O_{2}^{+} + e$$

$$N_{2} + hv \longrightarrow N_{2}^{+} + e$$

$$NO + hv \longrightarrow NO^{+}_{0} + e$$

Free ions and electrons do not survive for long in the lower part of the mesosphere as the density is comparatively high. They collide with other species to form neutral species. In the upper part of atmosphere, these species survive for long as the density of the atmosphere is low.

The ultraviolet radiations are not available during night, so the ions recombine with free electrons to form neutral species.

**Importance of atmosphere:** The following are the main advantages of the atmosphere which the nature has provided to living species.

(a) The atmosphere sustains life on earth and saves it from the hostile environment of outer space. It absorbs most of the cosmic rays from outer space and major portion of the electromagnetic radiations from the sun. It is able to transmit only near ultraviolet-visible, near infrared radiation (300–2500 nm) and radio waves (0.10–40.0μ) while filtering out tissue-damaging radiation.

- (b) The atmosphere maintains the heat balance of the earth by absorbing infrared radiations emitted by the sun and re-emitted from the earth.
- (c) The atmosphere is a source of oxygen which is essential for life on earth. It is required for respiration and combustion.
- (d) The atmosphere provides carbon dioxide which is essential for plant photosynthesis—carbon dioxide acts like a greenhouse by trapping the heat.
- (e) The atmosphere supplies nitrogen. Nitrogen is fixed by bacteria and electrical disturbances. The nitrogen compounds, thus, formed are essential for growth of plants. Nitrogen inertness reduces the activity of oxygen.
- (f) The atmosphere serves as a storehouse for water vapours which leads to rainfall activity.
- (g) The atmosphere helps in maintaining various natural cycles such as nitrogen cycle, oxygen cycle, CO<sub>2</sub> cycle, etc.

#### 2. HYDROSPHERE

The total water present on the earth in solid, liquid and gaseous phases constitutes the **hydrosphere**. Water covers 71% of the total surface of the earth. Earth is sometimes called a **water planet**. Hydrosphere includes all types of water resources such as oceans, seas, rivers, lakes, streams, reservoirs, glaciers, polar ice caps and ground water (*i.e.*, water below earth's surface). Approximately 97.3% of the world's vast supply of water is in oceans. Polar ice caps and glaciers provide 2% water while underground fresh water is hardly 0.6%. Fresh water lakes and rivers account for less than 0.01% of the total, yet they nevertheless, contain enormous amount of water  $(1.26 \times 10^{14} \text{ m}^3)$ . In vapour form, water is present only to the extent of 0.001%.

Water is essential to all forms of life. A man, on an average, consumes about 2.2 litre of water daily. More than 70% of the human's body mass is made of water. Plants cannot survive without water. Water is required for domestic uses, industrial cooling, power generation, transportation and waste disposal besides for drinking and agriculture (irrigation). The conservation and keeping up of a good supply of water is, thus, very essential.

**Sea water** is unfit for drinking or agriculture because each kilogram contains 35 g of dissolved salts. Most of the dissolved salts in sea water is sodium chloride, but more than 60 different elements are present in small amounts.

Sea water contains a number of dissolved gases, principally nitrogen, oxygen, carbon dioxide and noble gases. Nitrogen and noble gases are not utilised in any biological process. However, oxygen and carbon dioxide play important roles in marine environment. The sea plants photosynthesise and respire both. This process only occurs near the sea surface. The oxygen content decreases with depth. A minima occurs in the 200–1000 m depth range. Dissolved phosphates and nitrates act as fertilizers for **phytoplanktons** and other marine plants.

Snow and ice represent both a valuable asset and a menacing hazard. Snow is the principal source of water, not only in many of the world's mountainous areas, but also in the densely settled plains and valleys. Moreover, in the critical dry years, snow and ice are more dependable than other sources of water. The most detrimental effect of snowfall lies in the disruption of communication systems. Glaciers cause rock erosion also. In recent times, the ice caps of polar regions and glaciers have been greatly affected on account of the global warming.

Water for use in homes, agriculture and industry is generally obtained from lakes, rivers or underground sources. The water which we use for drinking purposes must be first purified to remove solid particles, colloidal particles, bacteria and other harmful impurities. Important steps for purification include preliminary filtration, sedimentation, sand filtration, aeration and sterilisation. The purified water still contains upto 0.5 g/L of inorganic ions such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, SO<sup>2+</sup>, F and HCO<sup>3</sup> but in such low concentrations these ions are not harmful. The circulation of water between hydrosphere, atmosphere, lithosphere and biosphere is called the **hydrological cycle**.

Water is an excellent solvent for many of the chemicals that make up our bodies, as well as for a wide variety of other substances. The importance of water as a slovent in living organisms and in the environment is given in the following points:

- (i) Blood plasma is an aqueous solution containing a variety of life-supporting substances. Inhaled oxygen dissolves in blood plasma in the lungs where O<sub>2</sub> combines with haemoglobin. Blood carries dissolved CO<sub>2</sub> to lungs to be exhaled from the body.
- (ii) Water transports nutrients into all cells and organs of our body.
- (iii) Water helps to maintain a chemical balance in the body by flushing waste products out.
- (iv) By dilution, water reduces the concentration of pollutants to safe levels or by carrying them away.
- (v) Plants take up nutrients from soil with the help of water. Water transports these materials into various parts of the plant.
- (vi) Rain water carries substances from atmosphere down to earth.

#### 3. LITHOSPHERE

It is the solid component of the earth consisting of soil, rocks, mountains, etc. It is the region which interacts with hydrosphere, atmosphere and biosphere. The earth comprises of three layers, *viz.*, **crust, mantle** and **outer** and **inner core.** The outermost solid portion, which is about 8–40 km above the mantle, is known as **crust.** The surface of the earth is covered with soil. It is the most important part of the lithosphere from the point of view of environment. Soil contains weathered

rocks as well as organic matter. It is a storehouse of minerals and is used for growing plants. The top layer is vital component since all the nutrients required by plants are present in this layer. A healthy soil always consists of micro-organisms such as bacteria, fungi, algae, protozoa, worms, etc. The top layer of the soil is actually the feeding zone of plants. Thus, the soil erosion must be avoided to maintain the fertility of the soil.

#### 4. BIOSPHERE

It refers to that part of the earth in which all life forms exist. Biosphere represents an interface between the non-living and the living. Biosphere extends from approximately 6 km above the sea level to about 10 km below the sea level. Living organisms and their non-living environment are inseparably interrelated and interact upon each other in an orderly manner so that there is continuous flow of energy and matter between them. Biosphere is equipped with certain special conditions which are necessary to support life. These conditions are:

- (i) A supply of air and water is available.
- (ii) A suitable temperature range exists.
- (iii) An area where the interface between lithosphere, atmosphere and hydrosphere exists is available.
- (iv) A supply of usable energy is available.
- (v) A supply of nutrients is available.

A community of organisms interacting with each other and with their non-living surroundings is called an ecosystem. Ecosystem may be small or large (Aquarium—small and tropical forest—large ecosystem.) Each ecosystem has its two parts: living and non-living, i.e., biotic and abiotic. Human activities can enhance the life supporting characteristics of the ecosystem or can degrade them as well.

Energy for the biosphere is provided through the action of photosynthesis. In this process, green plants use solar energy extract CO<sub>2</sub> and H<sub>2</sub>O from atmosphere and convert them into carbohydrates. The carbon is then said to be fixed by plants. The energy stored in the fixed carbon flows through the biotic community.

The elements needed by living organisms are of two types:

- (i) Macronutrients and (ii) Micronutrients.
- (i) Macronutrients: These elements are required in substantial quantities by living organisms. These elements are H, C, O, N, Ca, K, Si, Mg, S, P and Na. Carbon, hydrogen and oxygen are the main constituents of organic living matter. Nitrogen is contained in amino acids and proteins. Phosphorus, calcium and silicon are required for skeletal structure of vertebrates. Sodium and potassium play a role in regulating osmotic pressure in living cells. Magnesium is an essential constituent of chlorophyll and enzymes. Sulphur is the constituent of some of the essential amino acids.
- (ii) Micronutrients: These elements are required by living organisms in smaller quantities. These elements, however, are as vital as macronutrients. These are also called **tracer**

**elements.** Examples of tracer elements are: Al, Cl, Fe, Mn, Mo, etc. These elements play a specialised role in biochemical reactions such as photosynthesis and metabolism.

For terrestrial ecosystems, soil serves as a medium of entry of the nutrients into living organisms. Plants absorb their nutrients from the soil through their roots. With these they synthesise essential biomolecules upon which they, as well as other living species, depend.

**Biogeochemical cycles:** In order to maintain the biosphere and thus life, chemical elements must be recycled so that after use they become available again. A number of **biogeochemical cycles** or **natural cyclic processes** are taking place in the environment which keep a balance of the different materials present in the environment.

A biogeochemical cycle or natural cyclic process is defined as a process in which a material of the environment is consumed in some ways and then reproduced in other ways so that a balance of that material is maintained in the environment.

The following biogeochemical cycles are occurring in the environment.

- (i) Water cycle
- (ii) Carbon cycle
- (iii) Nitrogen cycle
- (iv) Oxygen cycle
- (v) Phosphorus cycle
- (v) Sulphur cycle, etc.

# 19:3 ENVIRONMENTAL POLLUTION AND ENVIRONMENTAL POLLUTANTS

The term environment as far as pollution is concerned, includes the air, the water and the land (soil). The pollution of our environment is one of the biggest hazards that humanity faces today. Pollution is a gift of industrial civilization. Progress in agriculture and industry have resulted into unlimited exploitation of every bit of natural resource. Such activities of man have adverse effect on all forms of living organisms in the biosphere. The unfavourable conditions created by man himself has threatened the survival not only of man himself but also of other living organisms. For the smooth growth and development of all living organisms, a balanced or natural environment is required which has been provided by nature. In balanced environment, the various components are present in a definite ratio and proportion. When the ratio of one or more components of the balanced environment is disturbed by natural happenings or human activities, it is said that the environment has been polluted.

Thus, any undesirable change of the physical, chemical or biological characteristics in the air, water and land which is harmful to man directly or indirectly through his animals, plants, industrial units or raw materials is termed environmental pollution.

Pollution may be natural or man-made (artificial).

(i) Natural pollution: It originates from natural processes. A few examples of natural sources of pollution are:

- (a) Volcanic eruptions; (b) Forest fires and coal mines fire; (c) Bacterial decomposition of agricultural matter; (d) Pollen grains of flowers; (e) Excreta of animals; (f) Floods; (g) Radioactive substances.
- (ii) Artificial pollution: It originates from the activities of man. Environmental deterioration by man is attributable to three major factors: (i) over-population (ii) urbanisation and (iii) industrialisation. The increasing amount of wastes generated by these three phenomena undoubtedly degrades the quality of land, air, water and food. When the waste products are not efficiently assimilated or decomposed or otherwise removed by the natural, biological and physical processes of the biosphere, adverse effects may result as the materials responsible for pollution accumulate or are converted to more toxic substances. Anything, if present in the environment in excess of permissible limits, causes pollution. The problem of pollution is very complex as one type of pollution will disturb and cause pollution in other systems also.

#### Pollution, thus, means:

- (i) The presence of anything in the environment in excess of required amount.
- (ii) Anything put into the environment which was not there in its natural state.
- (iii) Direct or indirect changes in one or more components of the ecosystem which are harmful to living organisms.
- (iv) Intentional or unintentional release of any chemical or geochemical substance in the environment with adverse, harmful or unpleasant effects.

Today everything is polluted. The air we breathe is polluted by automobile exhausts, industries, thermal power plants, etc. The fruits and vegetables are polluted due to the use of pesticides and insecticides and water in lakes and rivers has been polluted by wastes from chemical and other factories, by sewage due to uncontrolled population and use of plastic materials.

Although pollution is as old as man himself, but his awareness about it is only very recent. Concern over the state of environment has grown over since the sixties. The catastrophic events like the Bhopal gas tragedy, the Chernobyl nuclear reactor breakdown, etc., have given us a warning about the dangers of pollution. It is, thus, the duty of every citizen, every nation and every government to take concrete steps to minimise and control pollution.

#### **Pollutants**

Pollutants are chemical, biological or physical agents that exert undesirable effects on living organisms including human health, environment or belongings. According to "The Indian environment (Protection) Act 1986", a pollutant has been defined as any solid, liquid or gaseous substance present in such concentration as may be or may tend to be injurious to the environment. In a very simple way, a pollutant can be defined as a substance or an agent which causes pollution.

Various types of pollutants are listed below:

(i) Chemical agents:

Gases and particulates; Heavy metals; Pesticides; Petroleum; Solid and liquid wastes

(ii) Physical agents:

Heat; Odour; Noise; Radiation

(iii) Biological agents:

Micro-organisms; Population

Odum, in 1971, gave a different classification of pollutants. He divided them into two basic types from an ecosystem point of view.

- (a) Non-degradable pollutants: These are poisons like mercuric salts, aluminium cans, lead compounds, long chain phenolic chemicals, pesticides, etc. which either do not degrade or degrade very slowly in the ecosystem naturally. These are not recycled in natural environment. These substances are harmful even in low concentrations.
- **(b) Bio-degradable pollutants:** These are domestic wastes which can be rapidly decomposed under natural processes by micro-organisms. However, when accumulation of these occurs, *i.e.*, complete degradation does not take place, then these pollute the biosphere and create problems.

The various principal environmental pollutants are:

- (i) Deposited matter-Soot, smoke, tar, dust, grit, etc.
- (ii) Gases-Oxides of nitrogen (NO, NO<sub>2</sub>), sulphur dioxide (SO<sub>2</sub>), carbon monoxide, halogens, etc.
- (iii) Fluorides
- (iv) Acid droplets-Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), nitric acid (HNO<sub>3</sub>), etc.
- (v) Metals-Mercury, lead, iron, chromium, zinc, cadmium, nickel, tin, etc.
- (vi) Agrochemicals-Pesticides, herbicides, fungicides, bactericides, insecticides, weedicides and fertilizers, etc.
- (vii) Photochemical oxidants-Peroxyacetyl nitrate (PAN), peroxybenzoyl nitrate (PBN), aldehydes, ethylene, ozone, photochemical smog, etc.
- (viii) Petroleum and complex organic compounds.
- (ix) Sewage due to uncontrolled population and faulty urban planning.
- (x) Radioactive waste.
- (xi) Noise and heat.

# 19.4 SOME COMMONLY USED TERMS IN ENVIRONMENTAL POLLUTION

1. Contaminant: A substance which does not exist in nature but is introduced by human activity into the environment is called contaminant. It may or may not be harmful to the living organisms or non-living materials. The contaminant becomes pollutant when it has harmful effect. For example, methyl isocyanate vapours leaked from a defective tank killed many persons and caused respiratory, lung, eye and throat problems to others in Bhopal can be called contaminant, as it does not occur in atmosphere but it can be termed pollutant also as it

has dangerous effects. Generally, highly toxic materials are considered as pollutants.

- **2. Source:** The site from which the pollutants or contaminants originates is called source. The knowledge about the source is important because it helps to devise the methods to eliminate or minimise the pollutant.
- **3. Sink:** The material or medium which removes or interacts with a long lived pollutant is called sink. For example, oceans act as sink for atmospheric carbon dioxide and other water soluble gases. Limestone minerals act as sink for oxides of sulphur and sulphuric acid (acid rain).

$$\begin{array}{c} \text{CaCO}_3 + \text{SO}_2 \longrightarrow \text{CaSO}_3 + \text{CO}_2 \\ \text{CaCO}_3 + \text{SO}_3 \longrightarrow \text{CaSO}_4 + \text{CO}_2 \\ \text{CaCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O} \end{array}$$

- **4. Receptor:** Anything that is affected or spoiled by pollutants is called receptor. For example, marble structures are receptors of acid rain. Human beings are receptors of photochemical smog which causes irritation in the eyes and brings breathing problems.
- 5. Threshold Limit Value (TLV): The permissible limit of a pollutant in the atmosphere to which if a healthy person is exposed for 8 hours a day or 40 hours a week for life time, there is no adverse effect on him, is called threshold limit value. For example, TLV of CO is 40 ppm while that of CO<sub>2</sub> is 5000 ppm.

### 195 TYPES OF POLLUTION

The usual practice to classify pollution is on the basis of medium or component of the environment polluted. The common types of pollution are:

- 1. Air pollution
- 2. Water pollution
- 3. Soil or Land pollution

Sometimes, the classification is done according to the type of pollutant by which the pollution has been caused. The following types of pollution have been observed on this basis:

- (i) Air pollution
- (ii) Water pollution
- (iii) Soil pollution
- (iv) Noise pollution
- (v) Thermal pollution
- (vi) Radiation pollution
- (vii) Marine pollution
- (viii) Solid waste pollution
- (ix) Industrial pollution
- (x) Plastic pollution
- (xi) Oil pollution
- (xii) Soap and detergent pollution
- (xiii) Metal toxicity pollution
- (xiv) Smog pollution

In this unit, we shall study the first three types of pollution.

- (i) Air pollution
- (ii) Water pollution and
- (iii) Soil pollution

It is usually difficult sometimes to specify that a particular agent is an air pollutant, or a water pollutant or a soil pollutant. For example, a pesticide when sprayed might partly contaminate the air in vapour form, soil by adsorption and water running through a sprayed field.

### 19.6 AIR POLLUTION

Air is one of the most important constituents of man's environment. It has been calculated that a man breathes about 22,000 times a day inhaling about 16 kg of air by mass. Air is present everywhere. Air is essentially a mixture of gases. Due to the activity of living organisms, different gases in the atmosphere are found in a definite ratio and proportion. There is cycling of gases between the living organisms and atmosphere. It is due to organisms that oxygen and carbon dioxide are found in a balanced state in the atmosphere. Atmosphere maintains a narrow difference of day and night temperatures. It acts as a shield around the earth against lethal UV radiation and meteors. Without atmosphere, there will be no lightning, no wind, no clouds, no rains, no snow and no fire.

Air is the foremost susceptible component of our environment prone to pollution. Man has disturbed the favourable and natural air atmosphere in different ways, by removal of plants, by development of various industrial establishments, by burning of fossil fuels, etc. Pollution of air may have profound health effects and other consequences.

The composition of pure dry air has been given in section 19.2. Air pollution occurs when the concentration of a particular component of the air crosses the threshold limit value and becomes harmful.

Air pollution may be defined as any atmospheric condition in which certain substances are present in such concentrations that they can produce undesirable effects on man and his environment. According to WHO, air pollution may be defined as follows: "Substance put into air by the activity of mankind in a concentration sufficient to cause harmful effect to his health, vegetables, property or to interfere with the enjoyment of his property".

The study of air/atmospheric pollution mainly consists of the study of the two lower parts of atmosphere, *i.e.*, upto a height of about 50 km above the surface of the earth.

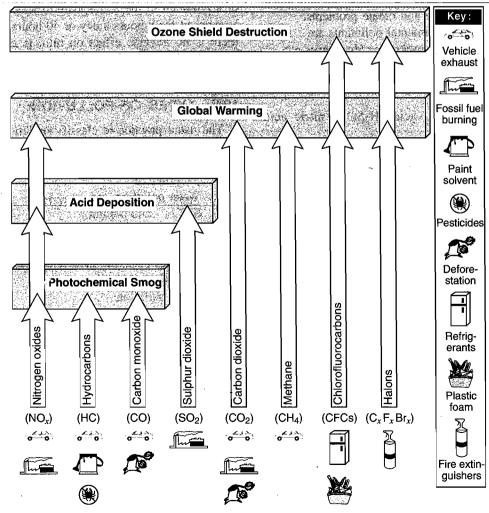


Fig. 19.1 Sources of air pollution and effects of air pollution

- 1. Tropospheric pollution
- 2. Stratospheric pollution

**Tropospheric pollution** is much more wide spread. The main pollutants of this sphere are gases such as oxides of nitrogen, oxides of sulphur, oxides of carbon, hydrogen sulphide, hydrocarbons, etc., and particulated matter such as dust, smoke, mist, fumes, aerosols, etc. Most of these substances are naturally present in definite proportions and are usually considered to be harmless but when their concentrations cross the threshold value limit, they become pollutants.

**Stratospheric pollution** is mainly due to depletion of ozone layer which may affect plants and human life adversely as UV radiations reach the earth.

#### Sources of air pollutants

There are two main sources of air pollution.

- **1. Natural sources :** The natural sources of air pollution are:
- (a) Volcanic eruptions emitting poisonous gases such as CO, SO<sub>2</sub>, H<sub>2</sub>S, etc.
- (b) Forest fires (caused by lightning)
- (c) Pollen grains dispersal
- (d) Bacterial decomposition of organic matter
- (e) Wind erosion of soil
- (f) Natural radioactivity, etc.
- 2. Man-made sources, i.e., sources due to human activities :

The human activities responsible for air pollution are summarised as:

- (a) Burning of fossil fuels such as coal, wood, etc.
- (b) Combustion of gasoline in the automobiles
- (c) Deforestation
- (d) Overpopulation
- (e) Fast industrialisation
- (f) Agriculture activities
- (g) Nuclear explosion, etc.

#### Air Pollutants

Air pollutants are classified into two types:

- 1. Primary pollutants
- 2. Secondary pollutants
- 1. Primary pollutants: These are harmful chemical substances which enter directly into the atmosphere as a result of natural and human activities. These include inorganic gases such as sulphur dioxide, carbon monoxide, hydrogen sulphide, nitric oxide, carbon dioxide, ammonia, hydrogen fluoride, etc., hydrocarbons and radioactive substances, particulate matter such as ash, dust, smoke, fumes, aerosols, etc.
- **2. Secondary pollutants:** These are harmful chemical substances which are formed by chemical interactions among primary pollutants and normal atmospheric constituents. For example, sulphur dioxide is a primary pollutant. It reacts with

oxygen in the atmosphere to form sulphur trioxide which further reacts with water vapours to form sulphuric acid.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Thus, sulphur trioxide and sulphuric acid are secondary pollutants.

The common secondary pollutants are:

NO<sub>2</sub>, HNO<sub>3</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, aldehydes, ketones, various nitrates and sulphates formed in soil, etc. The major processes that convert the pollutants from their primary forms to secondary forms are oxidation, dissociation and dissolution.

Reaction	Primary pollutant	Secondary pollutant
Oxidation	Sulphur dioxide	Sulphur trioxide
	Carbon monoxide	Carbon dioxide
	Hydrogen sulphide	Sulphur dioxide
Dissociation	Nitrogen dioxide	Nitric oxide + oxygen
	Oxygen (molecular)	Oxygen (atomic)
	Hydrocarbons and aldehydes	Organic radicals
Dissolution	Carbon dioxide	Carbonic acid
	Sulphur trioxide	Sulphuric acid
	Nitrogen dioxide	Nitric/Nitrous acid

#### Major Air Pollutants of Tropospheric Pollution

More than 90% of the air pollution (tropospheric pollution) is caused by the following five major pollutants.

- 1. Carbon monoxide (CO)
- 2. Oxides of sulphur  $(SO_X)$
- 3. Oxides of nitrogen (NO<sub>x</sub>)
- 4. Hydrocarbons  $(C_XH_Y)$
- 5. Particulates

Each of these pollutants is discussed one by one with respect to its sources, its harmful effects and methods to control it.

#### 1. Carbon monoxide (CO)

Carbon monoxide (CO) is a colourless, tasteless and odourless gas. It is 96.5% as heavy as air and is not appreciably soluble in water. It constitutes the single largest pollutant in urban atmosphere. It is highly toxic as it has a strong affinity towards haemoglobin of the blood and renders it ineffective in blood streams for oxygen supply. The gas is fatal over 1000 ppm, causing unconsciousness in an hour and death in four hours. If the gas is inhaled for few hours at even a low concentration of 200 ppm, it causes symptoms of poisoning. The accepted maximum allowable concentration (MAC) for occupational exposure is 50 ppm for 8 hours.

Carbon monoxide is generated by natural sources and man-made sources. Natural processes produce a larger amount of carbon monoxide than man-made processes.

- (a) Natural sources: The chief natural processes which contribute CO to atmosphere are:
  - (i) Volcanic eruptions
  - (ii) Forest fires

- (iii) Methane (an important and major constituent of natural gas and produced by bacterial decay of living or organic matter) on oxidation under controlled conditions gives CO
- (iv) Decomposition or degradation of chlorophyll.
- (v) The surface waters of western Atlantic ocean have been found to be supersaturated with CO. This is given to atmosphere. The production of CO in the ocean is biological. Marine algae and marine siphonophore produce carbon monoxide.
- (b) Man-made sources: The main sources are:
- (i) Incomplete combustion of fuels containing carbon: Approximately 80% CO comes from automobiles. In urban areas, it is observed that there is relatively high concentration of CO during peak hours. It has been estimated that for every litre of petrol by automobile about 370 g carbon monoxide is released as vehicular exhaust. The consumption of petroleum products and the number of automobiles are increasing at an alarming pace; thus CO levels will also increase and making the atmosphere as health hazard. Various forms of indoor combustion devices such as stoves, furnaces, gas fired heaters and charcoal braziers emit carbon monoxide.
- (ii) Carbon monoxide is ejected from waste disposal combustion, coal mines and power plants.
- (iii) Cigarette smoke contains about 2% carbon monoxide due to incomplete combustion of tabacco.
- (iv) Carbon monoxide is generated during several operations in iron and steel industry. Carbon monoxide is also a constituent of several industrial gases. For example, coal gas contains 5–10% CO and water gas contains 30–40% CO.
- (v) Agricultural waste burning contribute a considerable amount of carbon monoxide.

**Sinks of carbon monoxide:** Though natural processes and human activities are releasing large amounts of carbon monoxide in atmosphere, yet the level of CO in air does not rise too much. This is due to the presence of some natural sinks.

(i) Soil acts as an important **sink** for carbon monoxide. A number of soil bacteria such as *Methanosarcina barkerii* and *Methanobacterium formicum* are known to remove carbon monoxide. In the presence of these bacteria CO is either oxidised or converted into methane.

$$2CO + O_2 \xrightarrow{Soil} 2CO_2$$

$$CO + 3H_2 \xrightarrow{Soil} CH_4 + H_2O$$

**Note:** Urban areas face a greater threat of CO poisoning as the soil is covered by concrete and buildings and soil bacteria is not effective.

(ii) Some of the species such as hydroxyl (OH), perhydroxyl (HOO) radicals, atomic oxygen, ozone, nitrogen dioxide, etc., which exist in atmosphere can oxidise CO into CO<sub>2</sub>.

$$\begin{array}{c} \text{CO} + \overset{\bullet}{\text{OH}} & \longrightarrow \text{CO}_2 + \overset{\bullet}{\text{H}} \\ \text{CO} + \text{O} & \longrightarrow \text{CO}_2 \\ \text{CO} + \text{O}_3 & \longrightarrow \text{CO}_2 + \text{O}_2 \end{array}$$

(iii) The carbon monoxide may be transported from troposphere to stratosphere where it is readily oxidised into carbon dioxide by atomic oxygen, ozone, etc.

**Harmful effects of CO:** During breathing, the haemoglobin (Hb) present in the red blood cells combines with oxygen reversibly to form oxyhaemoglobin.

$$Hb + O_2 \longrightarrow HbO_2$$

The oxyhaemoglobin travels to the different parts of the body through arteries where it gives up oxygen and takes up CO<sub>2</sub> for return to the lungs where it is exhaled.

In case, the air which we breathe contains CO, it combines readily with haemoglobin (CO has 200 times more affinity than oxygen for haemoglobin). Due to formation of carboxy-haemoglobin (HbCO), the quantity of oxygen available to the body cells gets reduced, *i.e.*, carbon monoxide reduces the oxygen carrying capacity of the blood and this leads to oxygen starvation (anoxia). The deficiency of oxygen produces headache, drowsiness, choking, cardiac and pulmonary complications leading to paralysis and death.

- [(i) Smokers are more prone to anoxia. Pregnant women are advised not to smoke as increased CO level is injurious for unborn child.
- (ii) It is dangerous to sleep in a closed room with a coke fire burning inside during winter night.
- (iii) In case, carbon monoxide poisoning is detected well in time, the person can be treated by exposing him to oxygen under pressure (2-2.5 atm). Carbon monoxide of the carboxyhaemoglobin is replaced by oxygen and the victim may be revived.

$$HbCO + O_2 \longrightarrow HbO_2 + CO$$

Carbon monoxide has harmful effects on plants also when exposed for sufficient time. It reduces the nitrogen fixing ability of the bacteria. It also affects leaf drop, leaf curling, decrease in leaf size and premature ageing of the plants.

#### Control of Carbon Monoxide Pollution

The internal combustion engines in the automobiles are the primary sources of carbon monoxide emission. The engines emit a mixture of gases consisting of carbon monoxide, oxides of nitrogen, hydrocarbons and particulates. It is observed that if a particular method is used to control any one of these pollutants, than it results in the increase of other pollutants. For example, when air-fuel ratio (wt/wt) is 16:1, the emission of carbon monoxide and hydrocarbons is reduced but the emission of oxides of nitrogen increases. Thus, to minimize the emission of CO, suitable modifications are needed in the internal combustion engine or in the quality of the fuel. A few of these modifications proposed are as follows:

- (i) The carburettor is adjusted as to ensure proper air-fuel ratio. The presence of excess of air makes complete combustion of the fuel.
- (ii) Exhaust system is equipped with catalytic convertor which converts carbon monoxide into harmless products. Lead free gasoline is preferred these days as the catalyst gets easily poisoned by lead.
- (iii) Fuels such as CNG (condensed natural gas) and LNG (liquefied natural gas) which release minimum quantities of pollutants on combustion are advised to be used in place of gasoline.

#### 2. Oxides of sulphur (SOx)

Two common oxides of sulphur represented by the formula  $SO_X$  are sulphur dioxides ( $SO_2$ ) and sulphur trioxide ( $SO_3$ ). These are the most serious gaseous pollutants of the atmosphere. Both are colourless gases with pungent odour.  $SO_2$  is a primary pollutant while  $SO_3$  is a secondary pollutant:

**Sources:** 67% of the total amount of  $SO_2$  present in the atmosphere is released by **volcanic eruptions** (natural source) and remaining 33% is discharged due to human activity. The **man-made** sources of  $SO_2$  are:

(a) Coal combustion is the predominant man-made source of  $SO_2$  as its contribution is 60%. Coal contains 0.1 to 6% of sulphur. On combustion, this sulphur is oxidised to sulphur dioxide.

$$S + O_2 \longrightarrow SO_2$$

Coal is used in vast quantities in power plants and hence, power plants are largely responsible for release of  $SO_2$  into atmosphere.

- (b) Another contributor of sulphur dioxide is the combustion of petroleum and its products (20%).
- (c) It is also produced when sulphide ores like pyrites (FeS<sub>2</sub>), copper pyrites (CuFeS<sub>2</sub>), zinc blende (ZnS), galena (PbS), copper glance (Cu<sub>2</sub>S), etc., are roasted in air during extraction of respective metals.

$$2FeS2 + 5O2 \longrightarrow 2FeO + 4SO2$$

$$3Cu2S + 3O2 \longrightarrow 6Cu + 3SO2$$

$$2ZnS + 3O2 \longrightarrow 2ZnO + 2SO2$$

$$2PbS + 3O2 \longrightarrow 2PbO + 2SO2$$

(d) Hydrogen sulphide which is discharged into the air by natural processes is converted into SO<sub>2</sub> by oxidation in the atmosphere.

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2$$
  
 $H_2S + O_3 \longrightarrow H_2O + SO_2$ 

- (e) Many industries such as paper making, sulphuric acid manufacture, petroleum refining, etc., release SO<sub>2</sub> into atmosphere.
- (f) The sulphur dioxide persists in atmosphere for 2–4 days. During this time it is either dispersed to far away locations or oxidised to sulphur trioxide. The oxidation of sulphur dioxide can occur both photochemically or non-photochemically. In

the near ultraviolet region, the excited SO<sub>2</sub> molecules react with ozone (photochemical).

$$SO_2 + O_3 \xrightarrow{hv} SO_3 + O_2$$

Similarly, excited SO<sub>2</sub> molecules react with molecular oxygen.

$$2SO_2 + O_2 \xrightarrow{hv} 2SO_3$$

Non-photochemically, sulphur dioxide may be oxidised by molecular oxygen in presence of dust and soot particles.

$$2SO_2 + O_2 \xrightarrow{Particulates} 2SO_3$$

SO<sub>3</sub> immediately combines with moisture in atmosphere to form sulphuric acid.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$
 (Sulphuric acid)

The sulphuric acid formed comes down to the earth as acid rain.

Sinks of oxides of sulphur:  $SO_2$  is moderatory soluble in water forming a weak acid solution.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$
 (Sulphurous acid)

Oxides of sulphur are also converted into  $H_2SO_4$  (sulphuric acid). Both the acids in the form of acid rain come down on the earth where they meet with alkaline substances especially limestone minerals and sulphates are formed. In this way oxides of sulphur are removed from the atmosphere.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$
  
 $CaCO_3 + H_2SO_4 \longrightarrow CaSO_3 + H_2O + CO_2$ 

Thus, limestone minerals act as sink for oxides of sulphur. Harmful effects of oxides of sulphur: (i) Both SO<sub>2</sub> and SO<sub>3</sub> are highly irritating gases to respiratory tract of human beings and animals. Even at low concentration (about 5 ppm), it causes drying of mouth, throat and eye irritation. It brings breathlessness and affects larynx (voice box). Higher concentrations of SO<sub>2</sub> may cause lung disease and even lung cancer. SO<sub>3</sub> is more harmful than SO<sub>2</sub>.

- (ii) Sulphur dioxide has a very damaging effect on plants even at very low concentration (0.03 ppm). It affects plant growth and nutrient quality of plant products. Plants exposed to  $SO_2$  for sufficient time suffer from **Chlorosis** disease, *i.e.*, bleaching or yellowish of green portions of the leaves.
- (iii) The oxides of sulphur as such or in the form of acids (sulphuric acid and sulphurous acid) affect or damage a number of materials. For example,
- (a) Building materials such as limestone, marble, slate, etc., are damaged due to following reaction.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

- (b) Metals, particularly iron, are corroded.
- (c) Fading and deterioration of fabric, leather, paper and paints occur in the atmosphere having oxides of sulphur.

Control of  $SO_2$  pollution: The following methods can be applied to control  $SO_2$  pollution.

(i) By use of low sulphur content fuels such as natural gas or sulphur free fuels: A number of steps are being

taken to make coal sulphur free before it is put to combustion. The combined sulphur such as iron pyrites is removed by subjecting grounded coal to hydraulic washing. Iron pyrites, being heavier settle down while coal from pyrites floats on the surface and is collected. The free sulphur is removed by passing hydrogen gas over the fuel in presence of catalyst. The sulphur is converted into  $H_2S$  which is absorbed in a solution of diethanolamine.

(ii) By removal of oxides of sulphur from flue gases: The oxides of sulphur can be removed from flue gases by use of chemical scrubbers. The flue gases are passed through the scrubber containing slurry of limestone or lime.

$$\begin{array}{c} \text{CaCO}_3 + \text{SO}_2 \longrightarrow \text{CaSO}_3 + \text{CO}_2 \\ \text{CaCO}_3 + \text{SO}_3 \longrightarrow \text{CaSO}_4 + \text{CO}_2 \\ \hline \text{Ca(OH)}_2 + \text{SO}_2 \longrightarrow \text{CaSO}_3 + \text{H}_2\text{O} \end{array}$$

SO<sub>2</sub> can also be removed by the use of a solution containing citrate ions.

$$SO_2 + H_2O \Longrightarrow HSO_3 + H^+$$
  
 $HSO_3 + H_2Cit^- \Longrightarrow [HSO_3 \cdot H_2Cit]^{2+}$   
 $Complex$ 

Citrate ions are regenerated by use of H<sub>2</sub>S gas. Pure sulphur is obtained as a byproduct.

(iii) By using alternate sources of energy such as hydroelectric power plants and nuclear power plants instead of thermal power plants.

#### 3. Oxides of nitrogen (NO<sub>x</sub>)

Nitrogen forms a number of oxides, viz., nitrous oxide  $(N_2O)$ , nitric oxide (NO), nitrogen dioxide  $(NO_2)$ , dinitrogen trioxide  $(N_2O_3)$  and dinitrogen pentoxide  $(N_2O_5)$ . However, from the point of view of atmospheric pollution, the first three are important which are found in significant amounts in atmosphere. The normal global concentration of nitrogen oxides should be  $3 \times 10^{-3}$  ppm but the concentration in some cities is found as high as 2 ppm. Major sources of oxides of nitrogen in the atmosphere are as follows:

**Natural sources:** (i) Nitrogen comprises about 78% by volume of the atmosphere and oxygen as 20%. The two gases do not react with each other unless the temperature is very high. During thunderstorm and lightning, nitrogen and oxygen combine to form nitric oxide, which is further oxidised to nitrogen dioxide.

$$N_2 + O_2 \xrightarrow{\text{Electric}} 2NO$$
  
 $2NO + O_2 \longrightarrow 2NO_2$ 

- (ii) The oxides of nitrogen in atmosphere come from bacterial decay of organic matter by soil micro-organisms on the surface of the earth.
- (iii) Nitrous oxide is formed by the action of aerobic and anaerobic bacteria in the soil on nitrogen based fertilizers.

Man-made sources: (i) Combustion of fossil fuels such as coal, oil, natural gas, gasoline, etc., in automobiles and

power plants produces high temperatures at which nitrogen and oxygen combine to form nitric oxide and nitrogen dioxide.

(ii) Chemical industries involving manufacture of H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, produce oxides of nitrogen as byproducts which are released into atmosphere.

#### Harmful Effects of Oxides of Nitrogen

(i) Nitric oxide is biologically less active and less toxic than nitrogen dioxide. It does not have harmful effects on human beings and animals. However, it is readily converted into nitrogen dioxide by atmospheric oxygen. NO<sub>2</sub> is extremely toxic to living tissues. It can cause irritation in eyes, nose and throat. The oxides of nitrogen can cause viral infections. Higher doses of NO<sub>2</sub> are responsible for bronchitis and respiratory problems.

Like CO, NO combines with haemoglobin and reduces its oxygen transport efficiency.

- (ii) The oxides of nitrogen suppress the growth of plants and damage leaf tissues. Higher concentrations of NO (10 ppm) can cause decrease in photosynthesis.
- (iii) Sunlight decomposes NO<sub>2</sub> into NO and active oxygen atoms.

$$NO_2 \xrightarrow{Sunlight} NO + O$$

Active oxygen atoms react with traces of hydrocarbons present in the atmosphere and produce materials which are responsible for **photochemical smog.** The smog is a health hazard.

(iv) NO<sub>2</sub> combines with atmospheric moisture to form a mixture of nitric and nitrous acids.

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

These acids are carried to earth as acid rain. Acid rain reduces pH of the soil and thus reduces its fertility. The acid rain has a corroding effect on buildings and metallic structures.

(v) The oxides of nitrogen can cause fading of dyes used in colouring textiles.

#### Sinks of Oxides of Nitrogen

The oxides of nitrogen are not very stable. The average life of NO is 4 days and that of  $NO_2$  is 3 days. During this period, either the oxides are decomposed into  $N_2$  and  $O_2$  or converted into nitric acid through the following reactions:

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

Nitric acid comes down from the atmosphere to the surface of the earth in the form of acid rain. The acid reacts with bases to form nitrates.

Some natural processes and photochemical reactions also remove oxides of nitrogen in the atmosphere and serve as sinks.

#### Control of NO<sub>X</sub> Pollution

(i) The flue gases coming out from power plants or industrial units can be made from oxides of nitrogen and SO<sub>2</sub> by

scrubbing them with alkaline solutions of Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> or with sulphuric acid. The following reactions occur when H<sub>2</sub>SO<sub>4</sub> is used for scrubbing.

$$NO_2 + SO_2 + H_2O \longrightarrow H_2SO_4 + NO$$
  
 $NO + NO_2 \longrightarrow N_2O_3$   
 $N_2O_3 + 2H_2SO_4 \longrightarrow 2NOHSO_4 + H_2O$ 

The flue gases thus freed from  $NO_2$  and  $SO_2$  are released into atmosphere.

(ii) Catalytic converters are used in automobiles which convert the vehicular exhausts into free nitrogen and traces of ammonia.

#### 4. Hydrocarbons ( $C_XH_Y$ )

These are the chemical compounds of carbon and hydrogen only. These can be saturated or unsaturated, branched or straight chain or can have a ring structure. The most important hydrocarbons involved in air pollution are those which are volatile or in gaseous state under ordinary atmospheric conditions. The hydrocarbons in air by themselves alone cause no harmful effects. They are of concern because hydrocarbons undergo chemical reactions in the presence of sunlight and nitrogen oxides forming photochemical oxidants of which the predominant one is ozone. Methane is the main hydrocarbon present in atmosphere. The other hydrocarbons present are ethane, ethylene, acetylene, propane, n-butane, isopentane, toluene, n-pentane, m-xylene, isobutane, etc.

#### **Sources**

- (a) Natural sources: (i) Methane is emitted in large quantities during anaerobic decomposition of organic matter in soil, water and sediments.
- (ii) Forest fires and trees emit large amounts of hydrocarbons into atmosphere.
- **(b) Man-made sources:** (i) Incomplete combustion of fossil fuels in industry and thermal power plants and the exhaust of automobiles are releasing unburnt hydrocarbons into the atmosphere. This source contributes about 15% hydrocarbons.
- (ii) Solvents used in many industrial operations escape into air due to evaporation. This contributes about 10% to the total hydrocarbon pollution.

**Harmful effects:** (i) Hydrocarbons, particularly aromatic cause irritation in eyes, nose, lungs, etc. Hydrocarbons are carcinogenic, *i.e.*, they cause cancer.

- (ii) Hydrocarbons harm plants by causing ageing, breakdown of tissues and shedding of leaves, flowers and twigs.
- (iii) Methane is an important greenhouse gas which can trap 20 times more heat as compared to carbon dioxide.
- (iv) Hydrocarbons undergo chemical reactions in the presence of sunlight and oxides of nitrogen forming photochemical oxidants and photochemical smog which have highly harmful effects on human being as well as plants.

#### 5. Particulates or Suspended Particles

In general the term **particulate** refers to all atmospheric substances that are not gases, *i.e.*, they are minute solid particles or liquid droplets or mixtures of the two in air. Particulates can be composed of inert or extremely reactive materials of varying size. Particulate matter may be viable or non-viable. The viable particulates are the minute living organisms that are dispersed in the atmosphere. It includes bacteria, fungi, moulds, etc. The non-viable particulates are the different chemical substances which enter the atmosphere from various sources.

The size of the particulates ranges from a diameter of  $0.0002~\mu$  (about the size of a small molecule) to a diameter of about 500  $\mu$  (1  $\mu$  =  $10^{-6}$  m). The life-time of the particulates also ranges between a few seconds and several months. This life-time depends upon the settling rate which in turn is dependent on the size and density of the particles and the turbulence of the air. Particulates have the ability to act as sites for sorption. This property depends on the surface area which is large for most of the particulates. The process of sorption occurs when an individual molecule impacts on the surface of a particulate and does not rebound but sticks or sorbs.

**Sources of particulates:** There are four main types of non-viable particulate matter in the atmosphere. These are mists, smoke, fumes and dusts.

- (a) Mists: These are those particles that are produced by spray liquids and formed by the condensation of vapours in air. Examples, of this type can be portions of insecticides and herbicides that miss their targets and travel through the air.
- (b) Smoke: It contains very small soot particles which can be liquid or solid. These are produced by burning and combustion of organic matter. Oil smoke, tobacco smoke and carbon smoke are typical examples of this type.
- (c) Fumes: These are condensed vapours. Fumes of metals are the well known particulates of this type. These are normally released from chemical or metallurgical processes.
- (d) Dust: These are the fine particles formed by natural disintegration of rocks and soil or by mechanical processes of grinding, crushing, etc. Particles from soils and minerals contain calcium, aluminium and silicon compounds. Very small solid particles are carbon black, silver iodide combustion nuclei and sea salt nuclei. Larger particles are cement dust, soil dust, foundary dust, and pulverised coal. Liquid particulate matter generally categorised as "mist" includes rain drops, fog and sulphuric acid mist.

Thus both the natural and man-made sources contribute the airborne matter. The important natural sources are: (i) volcanic eruptions (ii) blowing of dust and soil by wind (iii) sea salt sprays (iv) forest fires (v) vegetation. The man-made sources are: (i) vehicular exhaust (ii) combustion processes (iii) metallurgical operations (iv) mining operations, etc. The given points are the **primary particulates.** 

Particulates produced in the atmosphere as a result of chemical reactions are called **secondary particulates.** These are formed either in gas phase reactions or by heterogeneous reactions between gases and already existing primary particulates. The majority of secondary particulates possess a diameter less than 1µ. The reaction leading to the formation of secondary particulates are largely catalysed by sunlight. The chief chemical reactants are sulphur oxides, nitrogen oxides, ammonia, water vapour and hydrocarbons.

#### **Some Common Particulates**

- (i) Soot: It is produced by incomplete combustion of carbonaceous fossil fuels such as coal, wood, natural gas, gasoline, etc., in low supply of oxygen.
- (ii) Fly ash: It comes from the combustion of high ash fossil fuels used in thermal power plants and smelters.
- (iii) Metal particles: These are released by various metal finishing operations. Micro particles of toxic metals are highly harmful.
- (iv) Metal oxides: These are produced by combustion of fuels with metallic compounds. For example, Fe<sub>3</sub>O<sub>4</sub> is produced by the combustion of coal containing iron pyrites.

$$3\text{FeS}_2 + 8\text{O}_2 \longrightarrow \text{Fe}_3\text{O}_4 + 6\text{SO}_2$$

(v) Lead salts: These come into atmosphere through exhaust gases from automobiles when lead tetraethyl  $[Pb(C_2H_5)_4]$  is used as antiknocking agent along with  $C_2H_4Cl_2$  and  $C_2H_4Br_2$  in gasoline.

$$\begin{aligned} \text{2Pb}(\text{C}_2\text{H}_5)_4 + \text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_2\text{H}_4\text{Br}_2 + 32\text{O}_2 &\longrightarrow \text{PbCl}_2 \\ &+ \text{PbBr}_2 + 20\text{CO}_2 + 24\text{H}_2\text{O} \end{aligned}$$

- (vi) Asbestos dust: Asbestos dust is introduced in atmosphere by industries manufacturing asbestos sheets, ropes, etc.
- (vii) Acid mist: Sulphuric acid and nitric acid mists are produced when oxides of sulphur and nitrogen dioxide come in contact with moisture.

$$2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4$$
  
 $4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$ 

(viii) Organic particulates: Paraffins, olefins and aromatic compounds particularly polycyclic aromatic hydrocarbons are emitted from petroleum refineries and automobiles. The polycyclic hydrocarbons are easily adsorbed on the soot particles and become serious health hazards.

#### Harmful Effects of Particulate Pollutants

(i) Effect on human beings: Small sized particulates which can pass through the nose and enter into lungs easily are highly dangerous. These particulates in lungs act as excellent sites for adsorption of carcinogenic compounds such as

polynuclear hydrocarbons and asbestos, etc., and bring lung diseases such as lung cancer, bronchital asthma and chronic bronchitis. The lung diseases are common in industrial workers.

Different types of particulates cause different types of lung diseases. For example,

- (a) Asbestos causes asbestosis.
- (b) Coal miners suffer from black lung disease.
- (c) Textile workers suffer from white lung disease.
- (d) Dust having free silica causes silicosis.
- (e) Beryllium compounds cause beryllosis.

Many biological particulates in the air, e.g., bacteria, fungal spores, pollen grains quite often cause allergy and bronchitis in man.

The following non-viable particulates exert adverse effects on human health.

- (a) Cadmium oxide Prostrate cancer, high blood pressure

  (b) Benzene Blood cancer (Leukemia)

  (c) Vinyl chloride Sarcoma of liver

  (d) Arsenic Lung, skin and liver cancer

  (e) Benzidine Bladder cancer

  (f) Lead particles Nervous diseases
- (ii) Effect on plants: Particulates deposit on the leaves of the plants. The common damage occurs in leaf structure such as *necrosis*, *chlorosis* and *epinasty*. They destroy chlorophyll and disrupt photosynthesis. Particulates block the stomata and retard the transpiration of minerals from the soil.
- (iii) Effect on materials: Large number of materials are damaged by particulates. Soot, dust, fumes, mists, etc., badly affect paints, clothes, buildings, sculptures, monuments, etc., corrosion of metals is accelerated in humid atmosphere. Particulates also damage electronic equipment.
- (iv) Effect on visibility: Particulates display optical properties which exert an important effect on air quality. They cause scattering and absorption of sunlight and reduce the visibility. They also produce blurring effect on vision.

#### Control of Particulate Pollution

The methods of control of particulates are based on settling or washing.

- (a) Gravity settling chamber: Effluent gases are allowed to enter a horizontal large rectangular chamber. The velocities of the gases decrease and the larger particles settle down under the influence of gravity.
- **(b) Wet scrubbers:** In this method, the effluent gases are allowed to enter a spray tower or chamber. A suitable liquid (generally water) is introduced in the form of a fine spray which washes away the particulates.
- **(c) Electrostatic precipitator:** It is the most effective and efficient method. The particulates are removed by installation of an electrostatic precipitator in the chimney. When a high potential is applied across the chimney, the carbon particles are

attracted by the charged electrodes. This results in the formation of soot which gets deposited in the chimney which is cleaned from time to time. Similarly, the particulates coming in the exhaust of automobiles are removed by catalytic converter.

In some of the industries, the filters are used to remove particulates. These filters work like the filters are used in air conditioners or vacuum cleaners. The exhaust gases are passed through them, leaving particulates and aerosols behind the filter.

#### Some other Air Pollutants

(a) Carbon dioxide ( $CO_2$ ): Carbon dioxide is a natural constituent of atmosphere and is vital for all forms of plant life. Normally, it forms about 0.03% by volume of atmosphere.

It is a colourless, odourless gas and is about 1.5 times heavier than air. Though it is non-poisonous, it does not support life as animals and human beings die in its atmosphere due to lack of oxygen. Carbon dioxide present in normal concentration is not an air pollutant. However, when CO<sub>2</sub> level increases in atmosphere, it results in global warming (called greenhouse effect-discussed later). Hence, it is considered to be pollutant in large amounts.

#### Major sources of CO<sub>2</sub> in atmosphere

- (i) Burning of fossil fuels like coal, natural gas and petroleum, etc.
- (ii) Industrial processes such as manufacture of lime, alcohol and other fermentation units.
- (iii) Biological decay of plants.
- (iv) In the process of respiration by animals, human beings and plants.

#### Sinks (Major consumers) of CO<sub>2</sub>

- (i) Green plants use CO<sub>2</sub> in presence of sunlight and chlorophyll to produce carbohydrates—photosynthesis.
- (ii) Oceans dissolve CO<sub>2</sub> to form carbonates, bicarbonates and organic compounds.

A balance of  $CO_2$  in the atmosphere is to be maintained. However, human activities have disturbed this balance and  $CO_2$  level in atmosphere is in increasing order. The increasing concentration of  $CO_2$  has changed global climatic conditions especially raising the global temperature.

- (b) Hydrogen sulphide (H<sub>2</sub>S): It is a colourless gas having smell of rotten eggs. It is extremely toxic and harmful even at low concentrations. The sources which release hydrogen sulphide into the atmosphere are:
  - (i) Natural decay of animals and vegetable matter
  - (ii) Volcanic eruptions
  - (iii) Industrial process like paper mills, oil refineries, chemicals manufacturing plants using sulphur.

#### **Sinks**

H<sub>2</sub>S is readily oxidised to SO<sub>2</sub> in the atmosphere.

$$H_2S \xrightarrow{O_2} SO_2 + H_2O$$

$$H_2S \xrightarrow{O_3} SO_2 + H_2O$$

It may combine with various metal compounds to form insoluble sulphides.

Mild exposure to  $H_2S$  can cause giddiness. In higher concentrations, it can be fatal. It is harmful to plants also as it affects leaves and reduces their growth.

(c) Chlorine (Cl<sub>2</sub>): Chlorine is a greenish-yellow coloured gas having disagreeable suffocating, poisonous and toxic gas. It does not occur as an air pollutant on a large scale. However, it can be highly dangerous on a local scale.

It is mostly released in the atmosphere by industrial processes from plastic industries, water treatment units and plants engaged in the manufacture of caustic soda.

In the atmosphere, chlorine dissolves in moisture to form hydrochloric acid and hypochlorous acid. These acids come down to the earth in the form of acid rain.

$$H_2O + Cl_2 \longrightarrow HCl + HClO$$

Chlorine causes irritation in mucus membrane. Exposure to chlorine for longer time may cause death.

- (d) Aldehydes: Out of the numerous aldehydes that may find their way into the atmosphere, only acrolein and formaldehyde have been detected in some areas with concentrations that may be toxic. Aldehydes are formed due to incomplete combustion of fossil fuels. These are also formed in the atmosphere by the interaction of hydrocarbons and oxides of nitrogen in presence of sunlight. The aliphatic and aromatic aldehydes are important precursors of the notorious peroxy-acyl nitrates (PAN) and peroxy-benzoyl nitrates (PBN) which act as photochemical oxidants.
- (e) Fluorides: Fluorides are present in the air of both rural and urban areas. The sources may be natural or industrial byproducts. Industrial processes of phosphate fertilizers, ceramics, aluminium, fluorinated hydrocarbons (freons-refrigerants aerosols, propellants, etc.), fluorinated plastics, etc., are the main sources of fluorides in atmosphere. These act as pollutants either in gaseous or particulate state. Freons when reach to upper atmosphere disturb the ozone layer.

#### **EFFECTS OF AIR POLLUTION**

### 19.7 ACID RAIN

The term 'acid rain' is used to describe all precipitations-rain, snow, fog, dew—which are more acidic than normal. The normal rain is slightly acidic having a pH of about 5.6 as carbon dioxide gas reacts with it to form a weak carbonic acid.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
 (Carbonic acid-weak acid)

As carbon dioxide is present in unpolluted air in traces the acidity is extremely mild and may be regarded as neutral. Acid rain, thus, refers to any precipitation which has pH less than 5.6. The pH of the acid rain can range between 5.6 and 3.5 and in some cases even lower upto 2.

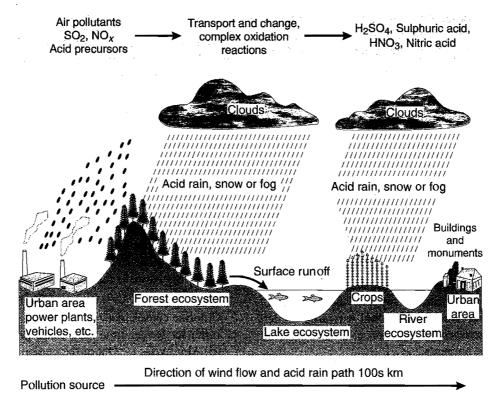


Fig. 19.2 Acid rain

Chemistry of acid rain: Acid rain results from the presence of two strong acids in polluted air: H<sub>2</sub>SO<sub>4</sub>, and to a lesser extent, HNO<sub>3</sub>.

Nitric acid comes largely from a three-step process. The first step involves the formation of NO from the elements by high temperature combustion, as in automobile engines or lightning in the atmosphere during the rainy season. This is then oxidised to NO<sub>2</sub> at normal atmospheric conditions. NO<sub>2</sub> combines with water to form a mixture of nitrous and nitric acids.

$$\begin{array}{c} N_2 + O_2 \xrightarrow{\mbox{High temp.}} 2NO \\ 2NO + O_2 \xrightarrow{\mbox{}} 2NO_2 \\ 2NO_2 + H_2O \xrightarrow{\mbox{}} HNO_3 + HNO_2 \end{array}$$

Coal, used in power plants, contains upto 4% sulphur, mostly in the form of minerals such as pyrite, FeS<sub>2</sub>. The combustion of coal forms sulphur dioxide. Petroleum products also on combustion release sulphur dioxide.

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$
$$S + O_2 \longrightarrow SO_2$$

Large quantities of SO<sub>2</sub> are also produced in the metallurgical processes used to treat sulphide ores.

$$2NiS + 3O_2 \longrightarrow 2NiO + 2SO_2$$

Natural processes such as volcanic eruptions, forest fires and bacterial decomposition of organic matter can produce the oxides of sulphur and nitrogen.  $SO_2$ , when it comes in contact with water, forms sulphurous acid ( $H_2SO_3$ ).

$$SO_2 + H_2O \longrightarrow H_2SO_3$$
 (Sulphurous acid)

SO<sub>2</sub> is partly and slowly converted into sulphur trioxide by molecular oxygen in presence of dust particles

$$2SO_2 + O_2 \xrightarrow{Dust particles} 2SO_3$$
  
 $SO_2$  is also oxidised to  $SO_3$  by ozone  
 $SO_2 + O_3 \xrightarrow{} SO_3 + O_2$ 

SO<sub>3</sub> thus formed readily combines with water and produces sulphuric acid as tiny droplets high in the atmosphere. These may be carried by the prevailing winds as far as 1500 km.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$
 (Sulphuric acid)

The sulphuric acid and nitric acid, thus formed remain as vapour under high temperature and begin to condense slowly as the temperature falls. These acids mix with rain or snow, *i.e.*, rain water gets acidified on its way down to the earth. The acidified rain water eventually mixes with the already existing water on the earth. The resulting pH determines the pH of the aquatic environment.

The presence of hydrogen sulphide and chlorine in the atmosphere also contributes to the formation of acid rain.

The acid rain is not confined to the regions where the harmful pollutants are emitted. Since winds carry atmospheric pollutants across national borders, the acid rain may fall hundred of miles away from the pollution sources.

#### Consequences of Acid Rain

- (i) Damage to animals: Acid rain causes lakes and rivers to become acidic and drop in pH can destroy the ecological balance. Most aquatic animals cannot survive when the pH is less than 4. Some species of fish such as salmon die even when the pH is less than 5.5. Certain species of algae and zooplankton are eliminated at pH less than 6. A reduction in the zooplankton and bottom fauna will affect the food availability for the fish population.
- (ii) Damage to plants: Acidic water is dangerous for plants. Leaf pigments are decolourised, *i.e.*, chlorophyll is affected and agricultural productivity is decreased. Several non-woody plants (such as barley, cotton) and fruit trees (such as apple, pear) are among the most susceptible to acid rain.

Many soils contain limestone and have natural buffering properties, but without this the acidified soil means plant nutrients are leached from the soil. Aluminium is released damaging root systems, seeds stop germinating, helpful soil organisms are killed.

$$\begin{array}{c} Al(OH)_3 + 3H^+ \longrightarrow & Al^{3+} + 3H_2O \\ \hline & Soluble \\ & (Toxic in nature) \end{array}$$

(iii) Material damage: Metallic surfaces exposed to acid rain are readily corroded. Textile fabrics, paper and leather products lose their material strength or disintegrate by the acid rain.

Building materials (limestone, marble, dolomite, mortar and slate especially) are weakened on reaction with acid rain as water-soluble compounds are formed. Thus, acid, rain is dangerous for historical monuments.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

The big industries emitting sulphur dioxide should not be established in urban areas and near the historical monuments.

(iv) Effect on human beings: Acid rain also affects human beings directly. The release of toxic metals held in rocks, especially aluminium, mercury and cadmium into water sources by acid rain can cause poisonous levels of metals to build in the fish which we eat. Acidic drinking water reacts with our water ducts and metal concentrations can cause damage to the kidneys and liver and diarrhoea in young children.

#### Ways to Minimise the Formation of Acid Rain

To reduce acid rain, sulphur dioxide emissions from power plants and smelters must be brought under control. The most direct approach is to remove sulphur from fossil fuels before combustion, but this is technically difficult to accomplish. A cheaper method is to remove SO<sub>2</sub> as it is formed. For example, in one process, powdered limestone is injected into the power plant furnace along with coal (Fig. 19.3). At high temperature, the following decomposition occurs:

$$\begin{array}{ccc} CaCO_3 & \longrightarrow & CaO + CO_2 \\ \text{Limestone} & & \text{Quick lime} \end{array}$$

The quick lime reacts with SO<sub>2</sub> to form calcium sulphite and some calcium sulphate.

$$\begin{array}{c} \text{CaO} + \text{SO}_2 \longrightarrow \text{CaSO}_3 \\ \text{2CaO} + 2\text{SO}_2 + \text{O}_2 \longrightarrow \text{2CaSO}_4 \end{array}$$

To remove the remaining SO<sub>2</sub>, an aqueous suspension of quick lime is injected into a purification chamber prior to the escape of gases through the smokestack.

$$Ca(OH)_2 + SO_2 + (\frac{1}{2}) O_2 \longrightarrow CaSO_4 + H_2O$$

One problem with this approach is that it produces large quantities of solid calcium sulphate as a waste product.

Quick lime is also added to lakes and soils affected by acid rain. This process is called **liming.** 

. Installing of a sulphuric acid plant near a metal ore smelting site is also an effective way to cut sulphur dioxide emission.

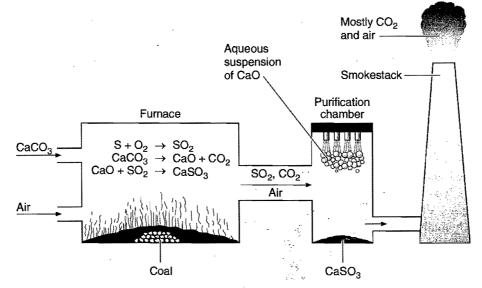


Fig. 19.3 Common procedure for removing  $SO_2$  from burning fossil fuel. Powdered limestone decomposes into CaO, which reacts with  $SO_2$  to form  $CaSO_3$ . The remaining  $SO_2$  then enters a chamber where it reacts with an aqueous suspension of CaO to form  $CaSO_3$ .

To do away with acid rain, an international programme, involving all the countries in order to take concrete measures to minimise sulphur dioxide pollution which travels very fast in atmosphere, is the need of the hour.

#### The Taj Mahal Protection from Air Pollution

Taj Mahal, one of the seven wonders of the world, situated at Agra, is losing its lustre day by day due to ill effects of air pollution mainly of acid rain. Agra and its adjoining areas such as Firozabad, Mathura, Bharatpur, etc., are having 2000 polluting industries. These include cast iron foundries, rubber manufacturing units, brick kilns, glass works and government owned petroleum refinery at Mathura. Due to rapid industrialization and increased growth of vehicular traffic, Agra city has abundance of oxides of sulphur and nitrogen in its atmosphere. These react with water vapour to form various acids which act on Taj's marble. As a result, there is continuous deterioration of this classical building which is the country's best loved landmark.

The government of India announced an action plan in 1995 to clean up the atmosphere which is affecting Taj Mahal. Marble of Taj Mahal must be guarded with protective coating which could resist the action of air pollutants. The industries located in nearby areas have been asked either to shift to other areas or to start using natural gas or liquefied petroleum gas for heating purpose. People living in the city have been advised to use LPG in place of coal, kerosene or firewood. If due protection of Taj is not provided then rapid weathering of its stone structure would occur.

### 19.8 SMOG

The word **smog** was coined to describe the combination of smoke and fog.

The name was proposed to describe the phenomenon which occured due to condensation of some kind of fog on the carbon particles present in the smoke produced due to combustion of fuels like coal and petroleum.

Smog is of two types:

- (i) Classical smog
- (ii) Photochemical smog
- (i) Classical smog: It is also called London smog or sulphurous acid smog. This was observed in London in 1952 and killed about 4000 to 5000 people. This type of smog is produced from gases like SO<sub>2</sub>, particulates and high humidity in the atmosphere. The particulates catalyse the oxidation of SO<sub>2</sub> to SO<sub>3</sub> which gets mixed with moisture in the tiny droplets of fog producing sulphuric acid drops which

condense on particulates of smoke or dust to give colloidal dispersion called smog.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$
  
 $SO_3 + H_2O \longrightarrow H_2SO_4$ 

This type of smog is usually formed during winter season in the early morning hours. However, after sunrise, its intensity increases due to photochemical oxidation of  $SO_2$  to  $SO_3$ . It occurs in the lower part of the atmosphere. It decreases visibility and is responsible for breathing troubles like bronchitis and asthma. It produces irritation to eyes, nose and throat. The London smog is also called **reducing smog** as it contains  $SO_2$  and carbon.

(ii) Photochemical smog: It is also called Los Angeles smog as it was observed for the first time in Los Angeles in 1950. This type of smog is formed by combination of particulates (smoke, dust, fog) with oxides of nitrogen and hydrocarbons in presence of sunlight. As photochemical reactions are involved in the formation of smog, it is called photochemical smog. It occurs in those areas which have warm, sunny and dry climate along with the atmosphere has large concentration of automobile exhausts. It usually occurs in the months of summer during the day time. Photochemical smog is characterized by brown haze of irritating nature. It is oxidising in character as it has high concentration of oxidants.

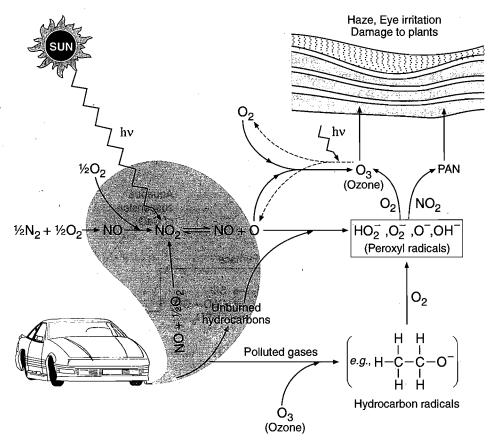


Fig. 19.4 Some main chemical reaction taking place in photochemical smog

Formation of photochemical smog: Smog begins with primary pollutants, substances that may be harmless and unreactive by themselves. Secondary pollutants, formed photochemically from the primary pollutants, are responsible for the buildup of smog. Primary pollutants consist mainly of nitric oxide, carbon monoxide and various unburned hydrocarbons.

Nitric oxide released into the atmosphere is quickly oxidised to nitrogen dioxide.

$$2NO + O_2 \longrightarrow 2NO_2$$

Sunlight causes photochemical decomposition of NO<sub>2</sub> (wavelength shorter than 400 nm) into NO and O.

$$NO_2 + hv \longrightarrow NO + O$$

Atomic oxygen is a highly reactive species that can initiate a number of important reactions, one of which is the formation of ozone.

$$O_2 + O + M \longrightarrow O_3 + M$$

where M is an inert gas such as nitrogen. It takes up the excess energy. Ozone attacks the C = C linkage in rubber.

where R represents groups of C and H atoms. In 'smoggy' areas, this reaction can cause automobile tyres to crack. Similar reactions are also damaging lung tissues and other biological substances.

A second process involving the participation of unburned hydrocarbons may be depicted as:

$$O + RH \longrightarrow R^{\bullet} + RCO^{\bullet}$$

$$RCO^{\bullet} + O_{2} \longrightarrow RCO_{3}^{\bullet}$$

$$RCO_{3}^{\bullet} + NO_{2} \longrightarrow RCO_{3}NO_{2}$$

$$(Peroxyacyl nitrate, PAN)$$

$$O \longrightarrow CH_{3}$$

PAN is a powerful lachrymator or tear producer and causes breathing troubles.

Extensive research has shown that carbon monoxide plays a very important role in the production of smog and the process is a dynamic one. When aldehydes are attacked by atomic oxygen, hydroxyl radicals are formed which lead to a series of reactions.

$$RCHO + O \longrightarrow RCO + OH$$
  
 $OH + CO \longrightarrow CO_2 + H$   
 $H + O_2 + M \longrightarrow HO_2 + M$   
 $HO_2 + NO \longrightarrow OH + NO_2$ 

The overall reaction is:

$$CO + O_2 + NO \longrightarrow CO_2 + NO_2$$

Fig. 19.5 shows a typical variation with time of primary and secondary pollutants. Initially, the concentration of NO<sub>2</sub> is quite low. As soon as solar radiation penetrates the atmosphere, the concentration of NO2 increase. The concentration of O3 remains fairly constant at a low level in the early morning hours. As the concentration of unburned hydrocarbons and aldehydes increases in the air, the concentrations of NO2 and O<sub>3</sub> also rise rapidly. The actual amounts, of course, depend on the location, traffic and weather conditions, but their presence is always accompanied by haze. The oxidation of hydrocarbons produces various organic intermediates, such as alcohols and carboxylic acids which are all less volatile than hydrocarbons. These substances eventually condense into small droplets of liquid. The dispersion of these droplets in air, called aerosols, scatters sunlight and reduces visibility. This interaction makes the air look hazy.

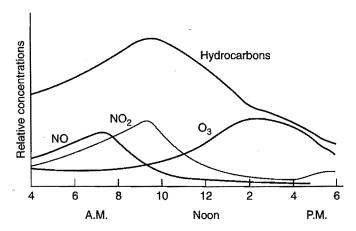


Fig. 19.5 Typical variation with time in concentration of air pollutants on a smoggy day

Effects of photochemical smog: The adverse effects of photochemical smog pose a potential threat not only to the local environment but to the far away places as well. Although photo-oxidants are formed mainly in highly industrialised and urban areas, the effect of smog can be observed even at a distance of 1000 km from the source region.

Smog is known to cause eye irritation, cough, chest discomfort and fatigue in humans. Peroxyacetyl nitrate is an etiological agent in the growing incidence of skin cancer. Ozone damages the membranes surrounding pulmonary capillaries.

Compared to human beings, vegetation is more prone to the harmful effects of oxidants. Ozone cause a reduction in plant growth. High concentrations of ozone damage forests. Organic oxidants act as poisons to plants.

Ozone may cause harm to fibres, dyes, paints and polymers. Natural rubber and synthetic polymers become brittle and crack.

Control of photochemical smog: Photochemical smog can be suppressed by the following technologies:

(i) Catalytic converters: The most straight forward way of reducing smog formation is to minimise the release of

oxides of nitrogen and hydrocarbons to the atmosphere. This involves installation of efficient catalytic converters in the automobiles. The harmful gases are converted catalytically into harmless gases. The limitation, however, is that catalytic converters work with unleaded petrol since lead poisons the catalysts.

A two way catalytic converter removes hydrocarbons and carbon monoxide from the exhaust. It consists of a mixture of platinum and palladium supported on ceramic or metal honey comb bed. It operates at an exhaust temperature of about 450°C and removes about 50% of the pollutants. Carbon monoxide is oxidised to carbon dioxide and hydrocarbons to carbon dioxide and water.

$$\begin{array}{ccc}
2\text{CO} + \text{O}_2 & \xrightarrow{\text{Catalyst}} & 2\text{CO}_2 \\
\text{HC} + \text{O}_2 & \xrightarrow{\text{Catalyst}} & \text{CO}_2 + \text{H}_2\text{O}
\end{array}$$

A three way catalyst removes hydrocarbons, carbon monoxide and nitrogen oxides from the auto exhaust. It is an example of oxidation-reduction catalysis.

$$2NO + 2CO \xrightarrow{\text{Catalyst}} N_2 + 2CO_2$$

$$2NO + CO \xrightarrow{\text{Catalyst}} N_2O + CO_2$$

$$2N_2O \xrightarrow{\text{Catalyst}} 2N_2 + O_2$$

$$NO_2 + HC^* \xrightarrow{\text{Catalyst}} N_2 + CO_2 + H_2O$$

$$NO + HC^* \xrightarrow{\text{Catalyst}} N_2 + CO_2 + H_2O$$

The three way catalyst consists of a mixture of platinum, palladium and rhodium deposited on a high surface area ceramic and metal honeycomb.

(ii) Chemical method: Photochemical smog can be suppressed by certain compounds which act as free radical traps. When these compounds are sprayed to the atmosphere, they generate free radicals which readily combine with free radical precursors of photochemical smog (such as  $O^{\bullet}$ ,  $R^{\bullet}$ ,  $RO^{\bullet}$ ,  $H^{\bullet}$  etc.). The compound diethylhydroxylamine, has been found to possess smog inhibiting characteristics. However, it produces an unpleasant odour.

### 19.9

# GREENHOUSE EFFECT AND GLOBAL WARMING

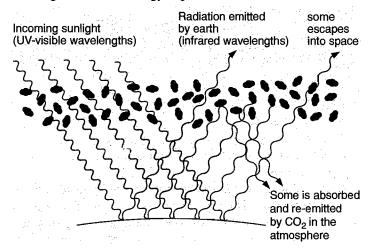
The greenhouse effect received its name because the earth's atmosphere acts much like the glass or plastic roof and walls of a greenhouse. Sunlight enters a greenhouse through the transparent glass or plastic and heat the plants but the heat emitted by the plants in the form of infrared radiation cannot pass through the glass or plastic roof and walls. As a result, the temperature inside the house increases. An effect similar to greenhouse is responsible for keeping the earth's surface warmer than it would otherwise be. Atmosphere around the earth acts like a glass of the greenhouse chamber. The gases present in atmosphere which are responsible for greenhouse effect are called greenhouse gases. The various gases which bring greenhouse effect are:

\*HC = Hydrocarbon

Carbon dioxide, water vapours, oxides of nitrogen, methane, ozone, chlorofluorocarbons, etc.

Although carbon dioxide is only a trace gas in earth's atmosphere with a concentration of 0.33 per cent by volume, it plays a critical role in controlling the climate of the earth. Without greenhouse effect, the average surface temperature of the earth would be about 35°C lower than it is today.

The major source of the earth's energy is the sun. About half of the radiant energy that strikes our atmosphere is either reflected or absorbed by the molecules that make up this envelope of the air. The sunlight that reaches the earth's atmosphere is ultraviolet, visible and infrared ranges between 100 and 5000 nm. However, UV radiations of shorter wavelengths are prevented from entering the troposphere by the presence of oxygen and ozone layer in the stratosphere. The rays that do reach the surface of the earth are largely in the visible and infrared (heat) regions. These radiations are absorbed by the earth and as a result, the continents and oceans are warmed. Warm bodies emit radiation and earth is no exception. Most of the radiation emitted by earth lies in the infrared region (wavelengths longer than 4000 nm). The rate at which energy escapes the surface of the earth is over twice the rate at which the planet directly absorbs energy from the sun. This means that the earth acts a little like an extravagant person. If this process were the only one to be occurring, the earth would be a very cold place. Fortunately, the planet does something extra to maintain the heat balance. Almost 84% of the heat radiated by the earth is absorbed by gases in the atmosphere and reradiated back to the earth's surface. As a result of this exchange, the total energy input from the sun balances the



**Fig. 19.6** The role of atmospheric CO<sub>2</sub> in the greenhouse effect. Carbon dioxide is transparent to incoming sunlight, but it absorbs and re-emits a significant amount of the infrared radiation emitted by the earth. This alters earth's energy balance, raising its average temperature

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energy output from the earth. A steady state is established, with more or less constant average terrestrial temperatures. It is the return of 84% of the energy radiated from the surface of the earth that has been termed the global greenhouse effect. (Fig. 19.6)

The constituents of the atmospheric greenhouse are made of molecules that are transparent to visible light, but absorb in the infrared region. Nitrogen and oxygen, the major components of the atmosphere are transparent to IR-radiations. However, some tracer gases in the troposphere are strong IR-radiation absorbers. These gases are carbon dioxide, water vapours, methane, ozone, chlorofluorocarbons, etc. These gases are transparent to sunlight, absorb IR-radiations emitted by earth and re-emit still longer wavelength IR-radiation, most of which return to the earth's surface where they are reabsorbed. This process keeps the temperature from falling dramatically at night when the ground is no longer absorbing energy from the sun.

The gases which are transparent to sunlight and are capable of absorbing IR-radiations and then re-emitting IR-radiations of longer wavelengths are termed greenhouse gases.

Upon receiving a photon in the IR region, a CO<sub>2</sub> or a H<sub>2</sub>O molecule is promoted to a higher vibrational energy level.

$$CO_2 + hv \longrightarrow CO_2^*$$
  
 $H_2O + hv \longrightarrow H_2O^*$ 

The energetically excited molecules soon lose their excess energy either by collision with other molecules or by spontaneous emission of radiation. Part of this radiation is emitted to outer space and the rest returns to the earth's surface keeping it comparatively warmer. The degree of temperature control depends on the amount of carbon dioxide and water vapour in the atmosphere. In desert regions, where the amount of water is very low and at high altitudes where the atmosphere is less dense, day and night temperature variations are much more severe than at lower altitudes having humidity. If it were not for the presence of these two relatively minor components of the atmosphere (CO<sub>2</sub> and H<sub>2</sub>O), the earth would be essentially barren of life. Its mean temperature would have been about -15°C, roughly 35°C lower than what it is today. In this way it can be said that CO<sub>2</sub> and H<sub>2</sub>O vapour act as an insulating blanket to prevent heat from escaping to outer space.

#### **Global Warming**

Whereas the total amount of water vapour in our atmosphere has not altered noticeably over the years, the carbon dioxide concentrations have risen by about 25% in the past century. This increase is as a result of extra burning of fossil fuels (petroleum, natural gas and coal) in order to meet the energy needs. Fig. 19.7 shows the increase in CO<sub>2</sub> concentration from the year 1958 to year 1992 (from 310 ppm to 360 ppm). The zig-zag line is a consequence of seasonal variation.

Other measurements indicate that during the past nearly 120 years, the average temperature of the planet has increased by somewhere between 0.4 and 0.8°C. Current estimates are that doubling the CO<sub>2</sub> concentration will result in a temperature increase of between 1.0 to 3.5°C. Recent estimates suggest that about half of the global warming may be attributable to

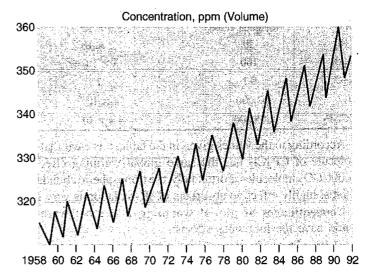
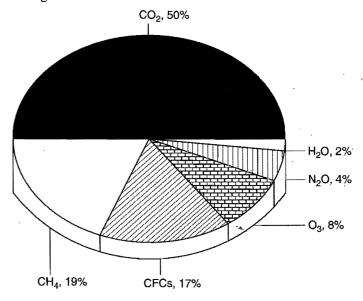


Fig. 19.7 Carbon dioxide levels (1958–1992) in the atmosphere are increasing exponentially

compounds other than carbon dioxide. Fig. 19.8 shows the relative contribution of various gases to greenhouse effect. The contribution of CO<sub>2</sub> is 50% while the contribution of other trace gases is also about 50%.



**Fig. 19.8** Relative contribution of radiatively active gases to greenhouse effect

The amount of warming which a greenhouse gas imparts to a square metre of the earth is called **radiative forcing**. The radiative forcing exerted by each greenhouse gas depends on its concentration and its ability to absorb long wavelength IR-radiation. The effectiveness is quantified by the greenhouse factor, a number that represents the relative contribution of a molecule of the gas to global warming. Values of the greenhouse factor for six common trace gases and their average concentrations in the troposphere are given in the following table.

Gas	Greenhouse factor	Tropospheric abundance (%)
CO <sub>2</sub>	1 (assigned value)	$3.6 \times 10^{-2}$
$CH_4$	' 30	$1.7 \times 10^{-3}$
N <sub>2</sub> O	160	$3 \times 10^{-4}$
$H_2O$	0.1	1
$O_3$	2,000	$4 \times 10^{-6}$
CCl <sub>2</sub> F <sub>2</sub>	25,000	$4.8 \times 10^{-8}$

According to the values given in the table, it is clear that one molecule of CF<sub>2</sub>Cl<sub>2</sub> has the same global warming effect as 25,000 CO<sub>2</sub> molecules. Fortunately, the tropospheric abundance of most highly effective absorbers of IR-radiation is very low.

Consequences of global warming: Global warming would have the following effects:

- (i) Rise in sea level: Although the temperature increase of 1 to 3°C may seem insignificant, it is actually large enough to disrupt the delicate thermal balance on the earth and could cause glaciers and ice caps to melt. Consequently, the sea level would increase. It has been estimated that the, sea level may rise 0.5 to 1.5 m in the next 50 to 100 years. Higher sea level would:
  - (a) increase the frequency and severity of floods
  - (b) damage coastal areas, *i.e.*, low lying areas would submerge
  - (c) cause loss of soil replenishment
  - (d) cause sea water intrusion into river and other aquatic systems near the oceans.

One third population of the world lives in low lying areas near the coasts. A large part of the population of some countries is at risk if sea level rises substantially.

- (ii) Evaporation of water from aquatic systems: Global warming will cause more water to evaporate from aquatic systems and increase the concentration of water vapour in the atmosphere. The extra water vapours will amplify warming because water vapours itself is a greenhouse gas.
- (iii) Changing patterns of rainfall: Patterns of rainfall would change worldwise causing large shifts in agriculturally productive areas.
- (iv) Effect on plants: Most plants record an increase in photosynthesis only initially when the concentration of CO<sub>2</sub> is high. But this trend tends to fall with time. It has been observed that plants grown in higher concentration of CO<sub>2</sub> have less nitrogen and more carbon content. The dead material of such plants do not provide nitrogen-based nutrients to plants and therefore, fail to increase soil fertility. Due to increase in temperature, the moisture content of soil would decrease, and thus reducing the fertility of the soil.

(v) Effect on human health and wild life: An increase in global temperature is likely to increase the occurrence of infectious diseases such as malaria, dengue, yellow fever, sleeping sickness, etc. Likewise, the population of mosquitoes, flies, snails will increase and these can be responsible for the outbreak of cholera, pneumonic plague, etc. Greenhouse effect shall seriously disturb wild life. With every rise of 1°C, plant and tree species will have to move 90 km polewards to survive. As trees and plants die out and habitats disappear, so will the animals that depend on them.

Steps to minimise greenhouse effect: (i) To combat greenhouse effect, the emission of carbon dioxide must be reduced. This can be done by improving energy efficiency in automobiles, household heating and lighting. Non-fossil fuel energy sources such as solar energy, wind energy, photovoltaic cells, etc., should be encouraged.

Worldwide, one-third of all carbon dioxide emissions come from thermal electric generating plants. This carbon dioxide can be injected into the ocean at depths below 500 m so that its chances of being released to the atmosphere are almost negligible. Recently, a process has been devised to convert CO<sub>2</sub> into fuel. It has been found that CO<sub>2</sub> reacts with water at 50°C in presence of TiO<sub>2</sub> as a catalyst and ultraviolet light to give methane, hydrogen and carbon monoxide. All of these products can be used as fuels.

- (ii) The production and use of chlorofluorocarbons must be banned. The phasing out of CFCs will help to slow down the warming effect. Other efforts, such as recovery of methane gas generated at landfills and the reduction of natural gas leakages, should be made.
- (iii) There should be a global effort to prevent the massive deforestation. Vegetation plays a vital role in maintaining the steady-state concentration of carbon dioxide in the atmosphere. Converting the forests to farmlands for crops and grasslands for cattle may do irreparable damage to the delicate ecosystem and permanently alter the climate pattern on earth. Thus, deforestation can be reduced by preserving the existing forests and growing more trees.
- (iv) The world's population, which at present is increasing at an alarming rate, must be stabilised. Many of our environmental problems are related to the expanding human population. The check on population is essential to stabilise the atmospheric burden of greenhouse gases.

# 19.10 OZONE LAYER AND ITS DEPLETION (STRATOSPHERIC POLLUTION)

The ozone layer in the stratosphere is a natural feature of the earth's environment. This layer exists between 20 and 35 km above the earth's surface. The layer shields the earth from the harmful ultraviolet radiation of the sun. In recent years, however, human activities have disturbed the ozone layer through an increase in the global concentrations of some atmospheric chemicals. A depletion of ozone layer is considered as a serious

threat to all forms of life. A 5% decrease in ozone concentration could increase the incidence of skin cancer by 20%. Ultraviolet radiation is also a factor in diseases of the eye, including cataract formation. It can cause genetic mutations and destory crops and other forms of vegetation.

UV-radiations between 180 nm to 360 nm coming from the sun are prevented by the ozone layer to reach the earth's surface. A photon with a wavelength between 180 and 240 nm breaks the  $O_2$  molecule into two atoms of oxygen.

$$O_2 + hv_{(\lambda=180 - 240 \text{ nm})} \longrightarrow O + O$$
 ....(i)

An oxygen molecule captures one of these oxygen atoms to form an ozone molecule.

$$M + O_2 + O \longrightarrow M^* + O_3 + \text{Heat.}$$
 ....(ii)

The second step occurs twice for each  $O_2$  fragmentation, giving the overall balanced process of ozone formation:

$$3O_2 + hv \longrightarrow 2O_3 + \text{Heat.}$$
 ....(iii)

The production of ozone is required both as a source of oxygen atoms and frequent collisions between the atoms and the molecules that make up the atmosphere. A high fraction of the atmosphere is oxygen atoms at high altitudes, but not enough collisions occur to form ozone in significant amounts. This is because at this altitude the pressure, the molecular density and the rate of molecular collisions are very low. Below 20 km, on the other hand, all the light energetic enough to split oxygen molecules into oxygen atoms has already been absorbed. Consequently, below this altitude, insufficient oxygen atoms are present to generate ozone. Therefore the ozone layer is between 20 km and 35 km above the earth's surface.

The formation of  $O_3$  goes on continuously, but  $O_3$  is also decomposed by UV-radiation between 240 and 360 nm.

$$O_3 + hv_{(\lambda = 240 - 360 \text{ nm})} \longrightarrow O_2 + O$$
 ....(iv)

The O atom can react with a second  $O_3$  molecule.

$$O + O_3 \longrightarrow 2O_2$$
 ....(v)

Net reaction

$$2O_3 \longrightarrow 3O_2$$
 ....(vi)

Short-wavelength UV-light forms O<sub>3</sub>. whereas long-wavelength UV-light decomposes O<sub>3</sub>. The reactions form a delicate balance in which the rate of O<sub>3</sub> decomposition matches the rate of O<sub>3</sub> formation, *i.e.*, a dynamic equilibrium exists and maintains a constant concentration of O<sub>3</sub>. Thus, the ozone layer absorbs nearly all the solar photons in the range 180 nm to 360 nm, *i.e.*, 90 to 95% energetic UV-radiation and protects life on earth.

#### Ozone Depletion

There has been much hue and cry about the destruction of stratospheric ozone and the issue has assumed global dimensions. Two scientists, who first suggested in 1974 that CFCs could deplete the ozone layer, **F. Sherwood Rowland** 

and **Mario Molina**, won the 1995 Nobel Prize in chemistry, along with **Paul Crutzen**, who suggested that oxides of nitrogen in the atmosphere could catalyse the decomposition of ozone.

(i) Ozone depletion by oxides of nitrogen: Over the past few years, the concentration of nitrous oxide has increased considerably in the atmosphere. This has been attributed to large scale combustion of fossil fuels and enhanced use of nitrogen fertilizers. Nitrous oxide and other oxides of nitrogen are also emitted by supersonic transport aircrafts. Though nitrous oxide is quite inert in the stratosphere, it is photochemically converted into more reactive nitric oxide.

$$N_2O + hv \longrightarrow NO + N$$
 ... (vii) ·

The nitric oxide so formed then undergoes the following chain reactions.

$$NO + O_3 \longrightarrow NO_2 + O_2$$
 ... (viii)

$$O_3 + hv \longrightarrow O_2 + O$$
 ... (ix)

$$NO_2 + O \longrightarrow NO + O_2$$
 ... (x)

Net reaction:  $2O_3 + h\nu \longrightarrow 3O_2$ 

Thus, in the presence of oxides of nitrogen in the stratosphere, the decomposition rate of  $O_3$  increases.

(ii) Ozone depletion by chlorofluorocarbons (CFCs) : Since the mid-1970s scientists have been concerned about the harmful effects of certain chlorofluorocarbons on the ozone layer. The CFCs which are generally called by the trade name Freons were first synthesised in 1930. Some of the common ones are CFCl<sub>3</sub> (Freon-11), CF<sub>2</sub>Cl<sub>2</sub> (Freon-12), C<sub>2</sub>F<sub>3</sub>Cl<sub>3</sub> (Freon-113) and C<sub>2</sub>F<sub>4</sub>Cl<sub>2</sub> (Freon-114). Because these compounds are readily liquefied, relatively inert, non-toxic, non-combustible and volatile. They have been used as coolants in refrigerators and air-conditioners. Large quantities of CFCs are also used in the manufacture of disposable foam products such as cups and plates, propellants and as solvents to clean newly soldered electronic circuits. Most of the CFCs used for commercial and industrial purpose are eventually discharged into the atmosphere. Because CFCs are highly resistant to chemical attack, they are very stable in the lower atmosphere, where they can exist for upto 100 years. This stability gives CFCs time to diffuse up through the troposphere into the stratosphere. There, CFCs absorb wavelengths between 175 nm and 220 nm that break carbon-chlorine bonds and produce chlorine atoms.

$$CF_2Cl_2 \xrightarrow{h\nu} CF_2Cl + Cl$$
 ... (xi)

$$CFCl_3 \xrightarrow{h\nu} CFCl_2 + Cl$$
 ... (xii)

The reactive chlorine atoms then undergo the following reactions.

$$Cl + O_3 \longrightarrow ClO + O_2$$
 ... (xiii)  
 $ClO + O \longrightarrow Cl + O_2$ 

Net Reaction :  $O_3 + O \xrightarrow{Cl} 2O_2$ 

<sup>\*</sup>M is an inert substance such as  $N_2$ . The role of M in this exothermic reaction is to absorb some of the excess energy released and prevent the spontaneous decomposition of ozone molecule.

The oxygen atoms in equation (xiii) are provided by the photochemical decomposition of molecular oxygen and ozone. In this mechanism, chlorine atoms catalyse ozone decomposition. One chlorine atom can destroy upto  $100,000 \, O_3$  molecules before it is removed by some other reaction. The above mechanism for the destruction of  $O_3$  has been supported by the detection of ClO in the stratosphere in recent years.

The catalysed decomposition of ozone is known to be responsible for the ozone hole that develops in **Antarctica** each year in September and October, at the end of winter in the southern hemisphere. No ozone is generated during the long, dark Antarctic winter. Meanwhile, a heterogeneous reaction occurring on clouds of ice crystals at -85°C produces species such as Cl<sub>2</sub>, Br<sub>2</sub> and HOCl.

$$CIO + NO_2 \longrightarrow CIONO_2$$
  
 $CIO + CH_4 \longrightarrow CH_3 + HCI$   
 $CIONO_2 + H_2O \longrightarrow HOC1 + HNO_3$   
 $CIONO_2 + HCI \longrightarrow Cl_2 + HNO_3$ 

When the sun reappears in September, these molecules decompose photochemically to form Cl or Br atoms.

$$HOCl \xrightarrow{h\nu} OH + Cl$$

$$Cl_2 \xrightarrow{h\nu} 2Cl$$

The reactive chlorine atoms are thus rendered free to deplete ozone. Ozone depletion is by no means restricted to the southern hemisphere. In the extremely cold winter of 1994–95, a similar 'ozone hole' was found in the Arctic. Beyond that, the concentration of ozone in the atmosphere over parts of Siberia dropped by 40%.

In 1987, an international treaty was signed in Montreal to cut back on the use of CFCs. Production of freon in the United States was stopped in 1996. If all the nations comply with the agreement, the amount of CFCs which was at the maximum level around the year 2000, will be slowly declining over the present century.

An intense effort is under way to find substitutes that are not harmful to the ozone layer. One of the promising substances is hydrochlorofluorocarbon-123 (CF<sub>3</sub>CHCl<sub>2</sub>). The presence of hydrogen atom makes the compound more susceptible to oxidation in the lower atmosphere, so that it never reaches the stratosphere. Unfortunately, the same hydrogen atom also makes the compound more active biologically than CFCs. It can cause tumours in rats, although its toxic effect on humans is not known.

#### Effects of Depletion of the Ozone Layer

(i) Depletion of ozone layer is a serious threat to mankind. On account of low concentration of ozone in the stratosphere, more UV-radiation enters into troposphere. UV-radiations lead to ageing of skin, cataract or blindness, sunburn, skin cancer, etc., UV-radiations can damage the immune system which may lead to increased viral infections.

- (ii) UV-radiations damage the plant proteins and chlorophyll. This leads to harmful mutation of cells. It also increases evaporation of surface water through the stomata of leaves and decreases moisture content of soil.
- (iii) Aquatic animals and aquatic plants are greatly affected by UV-radiations. Excessive exposure to radiations may kill many phytoplanktons and damage the fish productivity.
- (iv) Ozone depletion has a very strong effect on climate and ecology.
- (v) UV-radiations damage paints, fibres, etc.

#### **Global Warming and Ozone Depletion**

Global warming and ozone depletion are important environmental issues that involve the atmosphere. There are enough differences between the two phenomena which have been tabulated below:

	Global warming	Ozone depletion
Region of atmos- phere involved	Mostly troposphere	Stratosphere
Major substances involved	CO <sub>2</sub> , CH <sub>4</sub> , H <sub>2</sub> O, N <sub>2</sub> O	O <sub>3</sub> , O <sub>2</sub> , CFCs
Interaction with radiation	IR-radiation absorbed by molecules which vibrate and re-emits energy to earth	UV-radiation absorbed by molecules which are dissociated into smaller fragments
Nature of problem	Increasing concentrations of greenhouse gases are apparently increasing average global temperature	Decreasing concentration of O <sub>3</sub> is apparently increasing exposure to UV-radiation
Source of problem	Release of CO <sub>2</sub> from burning fossil fuels, deforestation	Release of CFCs
Possible consequences	Climate change; increase in sea level, change in agricultural productivity	Skin and eye diseases; growth of plants affected
Possible responses	Check deforestation and less use of fossil fuels	Production and use of CFCs be completely stopped

#### 19.14 WATER POLLUTION

Next to air, water is the important constituent of life-support systems. Water is the most important natural resource. 80% of the earth's area is occupied by water. However, hardly 2.5% makes up the total world's supply of fresh water including the frozen water in the polar ice caps and glaciers. Water is needed for irrigation, industry, domestic needs, shipping and for sanitation and disposal of waste. The conservation and keeping up of a good supply of water is thus very essential. Man has however, polluted much of this limited supply of water by industrial wastes, sewage and a number of synthetic chemicals. Many rivers of the world receive heavy flux of sewage, domestic waste, industrial effluents, agricultural wastes, etc., which

contain substances varying from simple nutrients to highly toxic materials. In our country, all the major rivers have been polluted. These have actually become an unending sewer fit only to carry urban liquid waste, half burnt dead bodies, pesticides and other wastes. Many of our lakes have become dark with foul smell. Moreover, the rainfall on its way down to the earth brings down the air pollutants. Polluted water is the water which has more negative qualities than it has positive ones, *i.e.*, it is no longer fit for any use.

Water pollution is the presence of any foreign substance (organic, inorganic, radioactive or biological) in water which tends to degrade the quality so as to constitute a hazard or impair the usefulness of water.

The common water pollutants are:

- (i) Oxygen-demanding wastes
- (ii) Disease causing agents
- (iii) Synthetic organic compounds
- (iv) Plant nutrients
- (v) Inorganic chemicals and minerals.
- (vi) Suspended solids
- (vii) Radioactive substances
- (viii) Thermal discharges
- (ix) Oil

(i) Oxygen-demanding wastes: Dissolved oxygen (DO) is essential for sustaining animal and plant life in any aquatic system. If the DO level in water decreases, the aquatic organisms may not survive. The wastes such as domestic, industrial and biodegradable organic compounds are oxygen demanding wastes, These are decomposed by the bacterial population which in turn decreases the oxygen from water.

BOD (biochemical oxygen demand) is a measure of the oxygen utilised by microorganisms during oxidation of organic materials. It is the most widely known measure for assessing the water pollution potential of a given organic waste. BOD is directly proportional to the amount of organic waste which is to be broken down.

The determination of BOD of a sample of water requires 20–30 days for the complete decomposition of organic waste present in the sample. This is too long time for obtaining data. Therefore, the time has been fixed as five days, *i.e.*, BOD is the amount of oxygen consumed in five days. The measurement is done at 20°C. The sample of water is saturated with oxygen. It is then incubated for five days at 20°C. Microorganisms utilise oxygen to oxidise the waste during this period. The remaining oxygen is

measured and subtracted from the amount of oxygen originally present to get the BOD value. It is expressed in ppm.

BOD is a real measure of water quality. Clean water has a BOD value of less than 5 ppm. The polluted river water could have a BOD value of 17 ppm or more. The untreated municipal sewage has BOD value of 100–400 ppm.

**Chemical oxygen demand (COD):** It is another important water quality parameter. It is an index of the waste (organic and inorganic) of water which can be oxidised by a strong oxidising agent usually acidified potassium dichromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. This reagent oxidises most of the substances present in water including those which are not oxidised by micro-organisms.

The water sample is treated with a known amount of acidic potassium dichromate solution. The unreacted potassium dichromate is determined by back titration with a suitable reducing agent like Mohr's salt. From the amount of  $K_2Cr_2O_7$  consumed, the amount of oxygen utilised in the oxidation of water sample can be calculated, with the help of following oxygen.

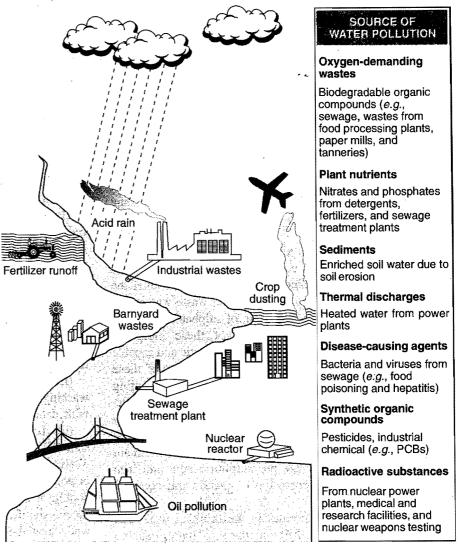


Fig. 19.9 Sources of water pollution

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

COD is also expressed in ppm. COD values do not necessarily match the BOD values. Textile wastes, paper mill wastes, etc., with high cellulose content have COD values considerably higher than BOD values as cellulose is not readily attacked by dissolved oxygen.

- (ii) Disease causing agents: These are the various pathogenic micro-organisms which may enter the water along with sewage or other wastes. These microbes, mainly bacteria and viruses, can cause various diseases such as cholera, typhoid, dysentry, gastroenteritis, polio, hepatitis, etc.
- (iii) Synthetic organic compounds: These include pesticides, detergents and other industrial chemicals. These chemicals when present in water can act as toxic poisons for plants, animals and humans. These chemicals enter the hydrosphere either by losses during their transport and usage or by accidental or intentional disposal of wastes from manufacturing units.

Polychlorinated biphenyls (PCBs), having high stabilities, are relatively new additions to the list of pollutants of water. They are used as fluids in transformers and capacitors. The presence of these PCBs in water causes skin disorders in humans. These act as carcinogenic.

- (iv) Plant nutrients: Nitrogen and phosphorus fertilizers which are drained from agricultural lands or from other sources into water bodies may stimulate the growth of algae and aquatic weeds. The excessive growth of algae and aquatic plants due to added nutrients is called Eutrophication. The anaerobic conditions created by the rotting algae can present a health hazard for birds, fish and other aquatic species. During the decomposition of aquatic plants by micro-organisms, the amount of dissolved oxygen decreases which proves fatal for aquatic species.
- (v) Inorganic chemicals and minerals: These include various metals and metallic compounds released from human activities or from natural minerals. These pollutants enter the water bodies from municipal and industrial waste waters and mine run-off. The acid-rain consisting of sulphate and nitrate ions makes the water acidic. Most of these inorganic compounds, particularly of heavy metals, are toxic and capable of killing living organisms in water bodies. Most of these substances produce physiological poisoning by becoming attached to the tissues of aquatic organisms and accumulate. The metals of concern are cadmium, chromium, lead, mercury and silver. Alkalies discharged by industries such as textiles, tanneries, paper, etc., can also destroy aquatic life. The main constituents of mine drainage are sulphuric acid and iron compounds. These cause corrosion of metals and concrete and are fatal to fish.

Recently the level of fluorides in the drinking water has considerably increased in different parts of India, causing **fluorosis** (an incurable bone disease).

- (vi) Suspended solids: Suspended solids in water are mainly of sand, silt and minerals eroded from the land. Solid particles settle in reservoirs and dams and thus reduce their water storage capacity. The suspended particles in water bodies also block the sunlight required for the photosynthesis by bottom vegetation and thus reduce the availability of food to fishes.
- (vii) Radioactive substances: The refining of uranium ore is an important source of radioactive waste producing radioactive materials containing radium, bismuth, etc., which are a hazard in drinking waters. Certain marine organisms have the capacity for accumulating radio nucleides from water. These may cause radioactivity in living organisms. Radioactive substances can enter humans through food and water. These may get accumulated in blood and certain vital organs such as liver, thyroid gland, bone and muscular tissues.
- (viii) Thermal discharges: Power plants and industries use large quantities of water for cooling purposes. Used water is usually discharged directly into water bodies. The temperature of water bodies thus increases. This brings down the DO level which is harmful for micro-organisms. An increase in temperature also increases the toxicity of some chemical pollutants. Poisons are more toxic in summer months.
- (ix) Oil: Oil and oil wastes enter rivers and other water bodies from several sources like oil refineries, storage tanks, automobile waste oil, petro-chemical plants and industrial effluents. Normal tanker operations and spillage from oil tanker accidents cause marine pollution and shore contamination.

Since oil is insoluble in water, it floats and spreads rapidly into a thin layer. At sea, the oil layer is responsible for the death of birds. The oil penetrates the birds' feathers thereby affecting their insulation and buoyancy. The birds experience difficulty in floating and flying. The oil layer on the surface of water reduces the DO levels in water as oxygen transfer from atmosphere is prevented. Oil may be driven to shores through wind and tides where it is accumulated and posses aesthetic problems.

#### **Control of Water Pollution**

- (i) Septic tanks should be used for each house. This will reduce the flow of municipal sewage and human excreta towards river, lake or pool.
- (ii) Rivers, lakes, etc., should not be used for bathing and washing purposes. In this way, water sources are not polluted with detergents and germs.
- (iii) Too much use of pesticides which are not degradable should be avoided. These are highly toxic substances.
- (iv) Efforts should be made to increase the use of low grade or polluted water. Treatment of domestic sewage for industrial cooling is a good example of efficient use. Water reuse has a special significance in mining and similar industries where the water availability is less. These efforts will save fresh water from being polluted.

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(v) Waste water treatment techniques should be applied before the polluted water enters a river, lake or pool. Available waste water treatment processes can be physical, chemical or biological. Physical processes comprise screening, sedimentation, floatation and filtration. Commonly used chemical processes are precipitation, coagulation and disinfection while biological processes are biological filtration and the activated sludge process. In particular cases, the processes such as carbon adsorption, oxidation and reduction, ion-exchange, reverse osmosis, electrolysis, etc., are also used.

# Water Quality Parameters (International standards for drinking water)

The quality of water is of vital concern for mankind as impure water can cause serious diseases. The following parameters must be followed before water is supplied for drinking purposes.

- It should be colourless and free from any odour or smell.
- (ii) It should be clear and free from suspended particles and turbidity. The turbidity should be less than 10 ppm.
- (iii) It should not be too acidic or too alkaline. The pH should lie between 5.5 to 9.5.
- (iv) It should be decent in taste. It can have some harmless salts for giving good taste. The total dissolved salts should not be more than 500 ppm.
- (v) It should be free from micro-organisms causing diseases.
- (vi) It should be free from harmful chemicals and should be reasonably soft.
- (vii) It should have dissolved oxygen 4-6 ppm.
- (viii) It should have specific conductance of  $300~\mu$  mho cm<sup>-1</sup>. Some international standards have been laid down for the drinking water. The chemicals that are allowed to be present and their tolerable limits permitted and some other conditions which must be satisfied for drinking water are briefly discussed below:
- (i) Fluoride: Water should be tested for fluoride ion concentration. Its deficiency is harmful as it causes tooth decay. Soluble fluoride is usually added to drinking water as to make its concentration upto 1 ppm or 1 mg dm<sup>-3</sup>. The F<sup>-</sup> ions make the enamel on the teeth much harder by changing hydroxyapatite, [3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·Ca(OH)<sub>2</sub>] into fluorapatite [3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·CaF<sub>2</sub>] which is much harder. However, brown mottling of teeth occurs if F<sup>-</sup> ion concentration exceeds 2 ppm. Higher concentrations (about 10 ppm) of F<sup>-</sup> ions are dangerous and cause harmful effects to teeth and bones.
- (ii) Lead: Lead pipes are used for water transport. If the water is comparatively acidic, lead salts come into water and get contaminated. The limit for the contamination of lead ions in drinking water is 50 ppb. Lead salts are slow poisons. They can damage liver, kidney and reproductive system, etc.
- (iii) Sulphate: At moderate concentrations of sulphate ions are harmless but excessive sulphate (> 500 ppm) in drinking water causes laxative effects and hypertension.

- (iv) Nitrate: The maximum limit of nitrate in drinking water is 50 ppm. Excessive concentration is harmful and can cause **methemoglobinemia** (blue baby syndrome).
- (v) Other metals: The recommended levels of some other metals in drinking water according to international standards are given in the following table:

#### Recommended Limits for Certain Substances in Drinking Water

	Contaminant	Permissible limit (ppm)
Chloride	(CI)	600
Cyanide	(CN <sup>-</sup> )	0.0001
Fluoride	(F <sup>-</sup> )	1–1.5
Nitrate + Nitrite	$(NO_3^- + NO_2^-)$	50
Phosphate	$(PO_4^{3-})$	0.1
Sulphate	$(SO_4^{2-})$	< 500
Arsenic	$(As^{3+})$	0.05
Chromium	$(Cr^{3+})$	0.05
Copper	(Cu <sup>2+</sup> )	3.0
Calcium	(Ca <sup>2+</sup> )	100
Magnesium	$(Mg^{2+})$	30
Barium	(Ba <sup>2+</sup> )	1.0
Iron	(Fe <sup>3+</sup> )	0.2
Lead	$(Pb^{2+})$	0.05
Zînc	$(Zn^{2+})$	5.0
Cadmium	$(Cd^{2+})$	0.005
Aluminium	$(Al^{3+})$	0.2
Manganese	$(Mn^{2+})$	0.05
Mercury	$(Hg^{2+})$	0.001
Pesticides		0.005

### 19.12 SOIL OR LAND POLLUTION

The soil or earth has been recognised as the mother of all plants, animals and human beings. It is very essential either directly or indirectly for the survival and maintenance of various biological species including man, as it produces food for all. The word soil is derived from a latin word *solum* meaning earthy materials in which plants grow. It is defined as a weathered layer of the earth's crust with living organisms and their products of decay. The chief components of the soil are inorganic matter (90–95%) and organic matter (5–10%). Besides, soil contains water and air. The composition of soil varies considerably from place to place.

Soil has become the dumping ground of most of waste products, *i.e.*, domestic, human, animal, industrial and agricultural. Every year the solid wastes dumped into the soil are increasing at an alarming rate all over the world. Different kinds of poisonous materials are being used these days and the whole earth is increasingly being poisoned and polluted as a consequence. The problem of soil pollution has aggravated by the use of agrochemicals such as pesticides, fungicides, insecticides, fertilizers and manures. Besides these, the soil is polluted by deadly pathogenic organisms.

Soil pollution is different from air and water pollution in the following respects:

- (i) Soil pollutants do not get dispersed unlike air and water pollutants. The pollution is localised unlike air and water pollution.
- (ii) The pollutants remain at a particular place for relatively longer periods.

#### Sources of Soil Pollution

The main sources of soil pollution are as follows:

- 1. Industrial wastes
- 2. Urban and domestic wastes
- 3. Agrochemicals
- 4. Soil erosion
- 5. Radioactive pollutants
- 6. Acid rain
- 1. Industrial wastes: Industrial wastes are the major cause of soil or land pollution. These wastes are mostly toxic due to the presence of cyanides, chromates, acids, alkalies, metals like nickel, cadmium, mercury, lead, etc. It is estimated about 50% of the raw materials used by the industries become waste products which are either thrown into water or dumped into the soil. The wastes are discharged from textile industry, paper and pulp industry, chemicals and drugs industry, soap and detergents industry, food processing industry, metal processing industries, glass, cement and engineering industries. The industrial wastes contain huge amounts of materials which are non-biodegradable and posing a serious threat to humanity.
- 2. Urban and domestic wastes: The urban and domestic wastes combined are referred as refuse. This comprises of garbage and waste materials like plastics, glass, metallic containers, fibres, papers and number of discarded products. The urban and domestic wastes are more harmful since most of these cannot be degraded easily. The wastes emit poisonous gases, toxic hydrocarbons and pathogenic microbes which cause diseases.
- **3. Agrochemicals:** The agrochemicals such as fertilizers, pesticides (insecticides, fungicides, herbicides), etc., are commonly used these days for agricultural crops. However, these find their way into food chain to be consumed by animals and humans and cause a number of health hazards.
- (a) Fertilizers: With the increase of population, there is an increasing demand of food. To enhance food production large quantities of fertilizers are being used.

No doubt, fertilizers certainly increase agricultural yield but their extensive use has adverse effects. Some adverse effects of fertilizers are: changes in mobility, status of nutrients in soil, stimulation of growth in crop fields and disturbance in ionic balance leading to high acidity, shortage of certain trace elements, etc. Excessive use of fertilizers results in the excessive growth of weeds and herbs.

Due to excessive amounts of nitrogen fertilizers, the concentration of nitrate ions increases in leafy vegetables.

Consumption of these vegetables results in bioaccumulation of nitrates in bodies. Nitrate by itself is not harmful but in human body it is reduced to nitrite which is responsible for occurrence of cancer.

**(b) Pesticides:** These are the chemicals which are used to save plants from pests, rats and parasitic fungi. Pesticides include **insecticides**, **fungicides** and **herbicides**. These substances cause soil pollution and adversely affect the health of animals and human beings.

According to a survey made by WHO, more than 50,000 people in developing countries are affected and poisoned annually and about 5000 die as a result of the effects of toxic agents used in agriculture. Samples of fruits, vegetables, milk and eggs from various parts of India showed that they contain pesticide residues much higher than human tolerance limits. Pesticides not only bring toxic effects on animals and human beings but also alter the fertility and decrease the soil respiration (root respiration and microbial respiration). Soil moisture has also been significantly reduced by pesticide application.

(i) Insecticides: These are the chemicals used to kill insects which damage the crops. After World War II, DDT was used in agriculture to control the damages caused by insects, rodents, weeds and various crop diseases. Other common examples of insecticides are BHC (benzene hexachloride), aldrin, dieldrin, etc. These insecticides are persistent in the environment and show biological activity for long periods of time. However, these insecticides not only kill unwanted insects but also target organisms which are helpful to crops. These insecticides keep on accumulating in the environment and cause pollution as being non-biodegradable. Their repeated use produces resistance in the pests. They are harmful to human beings and have been phased out. Consequently, a new series of insecticides, namely organophosphates, carbamates and pyrethroids have been introduced. Organophosphates and carbamates are biodegradable. But these are nerve toxins and are harmful to humans and have caused even deaths. Pyrethroids are neither presistent nor toxic, though costly.

It is not possible to ban the use of insecticides but the best option is to search for alternative insecticides which will kill pests but are friendly to environment.

- (ii) Fungicides: These are the chemicals which inhibit or prevent fungal growth or fungal diseases in plants or their seeds. Organomercury compounds are the most common fungicides. However, mercurial fungicides are responsible for human poisoning and deaths. The fungicides in the soil increase the number of harmful bacteria and decrease the population of useful types. For example, application of 4,6-dinitro-*o*-cresol and captan prevent nodule bacteria from initiating symbiotic nitrogen fixing process. The best fungicide available today is a derivative of β-methoxyacrylic acid.
- (iii) Herbicides: These are the chemicals used to control weeds. Some common weeds killers used earlier were inorganic compounds namely, sodium chlorate (NaClO<sub>3</sub>) and sodium

arsenite (Na<sub>3</sub>AsO<sub>3</sub>). However, their use has been restricted as they are toxic to mammals. These days, organic herbicides such as **triazines** are widely used.

- **4. Soil erosion:** Top soil is the most important as all agricultural activities depend on it. It is the vital component since all the nutrients required by plants are present here. At times, if it so happens that the top soil is dissipated by water or wind, the situation is termed **soil erosion.** Such soil becomes unsuitable for vegetation or agricultural production. Soil erosion is a natural process. It is caused by flow of water over the fields and by wind. The following factors influence the rate of soil erosion.
  - (a) Deforestation and loss of vegetation
  - (b) Cultivation on slopes of mountains
  - (c) Soils with low organic content.

Roots of grasses are an excellent binding material and keep the soil intact. Over-grazing, over-cropping and improper tilling accelerate soil erosion.

- 5. Radioactive pollutants: Radioactive wastes are produced in nuclear reactors, laboratories and hospitals. Nuclear explosions also produce a large number of radioactive wastes. Dumping of nuclear wastes is the biggest problem. From the soil, radioactive substances pass on to the human beings and animals in the form of food. The radioactive substances emit rays which are extremely harmful to human and animal cells.
- **6. Acid rain :** Acid rain disturbs the fertility of the soil. The activity of symbiotic nitrogen fixing bacteria present in the nodules of leguminous family is inhibited. The acid rain makes the soil acidic. This adversely affects the plants and animals. The acid rain contains H<sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub> ions which leach the nutrients from the soil. Acid rain is responsible for damaging forests and other vegetations.

**Control of soil pollution:** The following steps have been suggested to control the soil pollution:

- (i) The use of chemical fertilizers can be reduced by applying biofertilizers and manures. Biological methods of pest control can also reduce the use of pesticides and thereby minimise soil pollution.
- (ii) Recycling and recovery of materials appears to be a reasonable solution for reducing soil pollution. Materials such as paper, glass and some kinds of plastics can be recycled. This would decrease the volume of refuse and help in the conservation of natural resources. For example, recovery of one tonne of paper can save 17 trees.
- (iii) Control of land loss can be attempted through restoring forest and grass cover to check soil erosion and floods. Crop rotation or mixed cropping can improve the fertility of the land.
- (iv) Proper methods should be adopted for the disposal of solid wastes. The simplest and most widely used technique of solid waste management is to bury the waste in locations situated away from residential areas. While adopting this practice, environmental and aesthetic considerations must be taken into consideration before selecting the dumping sites.

Acidic and alkaline wastes should be first neutralised, the insoluble material if biodegradable should be allowed to degrade under controlled conditions before their disposal. Incineration of wastes is expensive and leaves a huge residue and adds to air pollution. Pyrolysis, a process of combustion in absence of oxygen or the material burned under controlled atmosphere of oxygen, is an alternative to incineration. The gas and liquid thus obtained can be used as fuels. Pyrolysis of carbonaceous wastes, like firewood, coconut, palm waste, corn combs, cashew shell, rice husk, paddy straw and saw dust, yields charcoal along with products like tar, methyl alcohol, acetic acid, acetone and a fuel gas. Dung should be used to produce "gobar gas" and good manure through gobar gas plants.

## 19.13 STRATEGIES TO CONTROL ENVIRONMENTAL POLLUTION

Environmental pollution affects human beings, animals, plants as well as materials. It does not only slow down growth of plants or bring diseases to human beings and animals but can cause havoc. Every individual should be aware about dangers of environmental pollution and must try to minimise them by proper and scientific planning. If we do not act now, it is certain that not only this generation but the generations to come will suffer immeasurably. Following are some suggestions which can help to minimise pollution:

- (i) Population control is the foremost thing. Uncontrolled growth of population is the major threat to environment.
- (ii) Vegetation checks pollution. Forests should be maintained properly. Their areas should be increased. Green belts in cities (especially the industrial ones) should be developed.
- (iii) Non-conventional methods of producing energy should be developed. The use of fossil fuels should be reduced as far as possible.
- (iv) Proper sewage disposal plants and recovery of sewage water for various industrial and domestic purposes should be established.
- (v) Domestic garbage should be profitably utilised. Gobar gas plants in rural areas should be installed.
- (vi) Manures and biofertilizers should be used in place of chemical fertilizers.
- (vii) To reduce the volume of refuse, the recycling processes should be developed.
  - (viii) All types of nuclear tests must be stopped.
- (ix) The chimneys of industries should be placed at greater heights. These should be fitted with filters. The industrial wastes must be first treated to remove the hazardous materials before discharge.
- (x) There should be strict laws to prevent pollution. Heavy fines should be imposed on defaulters.

There are two types of wastes which are causing environmental pollution.

(a) Household waste which includes mainly sewage and municipal garbage.

(b) Industrial wastes include inorganic and organic suspended particles and inorganic and organic soluble matter. Some of them may be toxic in nature.

The proper disposal of these wastes can save the environment from pollution. Some of the methods which are usually employed for the disposal of these wastes are given below:

- 1. Recycling: This is the simplest method for waste disposal as a number of waste materials can be used as raw materials to manufacture of useful products again. Examples of recycling by industry are:
  - (i) The collection and recycling of glass
  - (ii) The use of scrap metal in the manufacture of steel
  - (iii) The recovery of energy from burning combustible waste.
- (iv) Due to recent developments, clothes will be made from recycled plastic waste.
  - (v) The use of waste paper.

Thus, recycling saves the cost of raw materials and converts waste into wealth.

- **2. Sewage treatment :** The treatment of sewage involves the following stages:
- (i) First stage involves the removal of large solid particles. This is done by mechanical process consisting of screening and sedimentation. The waste is filtered through different types of screens. The solids that are removed are disposed of in landfill sites.
- (ii) It is then allowed to flow into sedimentation tanks. This step allows the removal of solids that settle out (called **sludge**). This also allows the removal of grease which floats to the surface and can be skimmed off.
- (iii) Next stage involves the biological oxidation of organic content of waste materials by micro-organisms followed by filtration.
- (iv) In the final stage, some specialised physical and chemical processes are applied to remove the specific pollutants which are still present in order to improve the quality of waste water. The processes used are chemical removal of phosphate, coagulation, treatment with activated charcoal, disinfection by chlorine, reverse osmosis, filtration, etc.

Sludge is produced during above operations. It is dried and then may be incinerated, digested or dumped.

#### Incineration

It converts organic matter into CO<sub>2</sub> and H<sub>2</sub>O. It is used to destroy household waste, chemical waste and biological waste (e.g., from hospitals). A high temperature usually above 1273K and a plentiful oxygen supply is required. Exhaust gases must be filtered. The process leaves ash behind which is disposed of as landfill. The main disadvantage of this process is that it causes air pollution.

#### Digestion

The sewage sludge can undergo anaerobic digestion when micro-organisms degrade wastes in absence of oxygen. This process can also be applied to degrade a variety of toxic organic compounds. The overall process is the conversion of the organic materials into carbon dioxide and methane.

$$2(CH_2O) \longrightarrow CO_2 + CH_4$$

Methane may be used as a fuel.

#### Dumping

Dumping of the sewage sludge into sea has been very common. However, dumping of the sludge into land is increasing now-a-days. This is because it contains compounds of nitrogen and phosphorus which act as fertilizers for the soil.



# GREEN CHEMISTRY AS AN ALTERNATIVE TOOL FOR REDUCING POLLUTION

Over the past decade, an important initiative known as Green chemistry, the use of chemistry to prevent pollution, has been taken. "Green chemistry" can be defined as the design, development and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and environment. Green chemistry reduces pollution through fundamental break throughs in designing and redesigning chemical processes with an eye towards making them environmentally friendly, that is "benign by design". In this regard, Dr. Barry Trost advocates an 'atom economy' approach to the synthesis of commercial chemical products such as pharmaceutical, plastics and pesticides. Such synthesis would be designed so that all reactant atoms end up as desired products, and not as wasteful byproducts. This approach would save money as well as materials and undesired products would not be produced as waste which requires disposal. The reason green chemistry being adopted so rapidly around the world is because it is a pathway to ensuring economic and environmental prosperity.

The main objectives of green chemistry can be summarised in the following points:

- (i) It is better to prevent waste than to treat or clean up waste after it has been created.
- (ii) Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product.
- (iii) Whenever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and environment.
- (iv) Chemical products should be designed to affect their desired functions while minimising their toxicity.
- (v) The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- (vi) Energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimised. If possible, synthetic methods should be conducted at ambient temperature and pressure.

- (vii) A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- (viii) Unnecessary derivatization should be minimised or avoided if possible because such steps require additional reagents and can generate waste.
- (ix) Catalytic agents as selective as possible should be used.
- (x) Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- (xi) Substances and the form of a substance used in a chemical process should be chosen to minimise the potential for chemical accidents, including releases, explosions and fires.

Innovative "green" chemical methods already have made an impact on a wide variety of chemical manufacturing processes by decreasing or eliminating the use or creation of toxic substances. For example cheaper, less wasteful and less toxic methods have been developed to produce ibuprofen, pesticides, new materials for disposable diapers and contact lens, new drycleaning methods and recycled silicon wafer for integrated circuits. Some examples of green chemistry are given below:

- (i) Halons are greenhouse gas compounds composed of carbon, fluorine and bromine. These are used in fire fighting and other applications. Using a green chemistry approach, Pyrocool Technologies has synthesised a halon substitute. The product, called Pyrocool, is an environmentally benign foam that is more effective than halons in fire fighting, even large scale fires such as those on oil tankers and jet airplanes can be extinguished in a short time.
- (ii) Chlorofluorocarbons have been in use in refrigerators and air conditioning plants. However, these compounds have been found to be unfriendly to environment. These compounds are responsible for depletion of ozone layer in stratosphere and for global warming. Substitutes to these compounds such as HFC-134a (CF<sub>3</sub>·CH<sub>2</sub>F) have been discovered which are considered to be more friendly to environment.
- (iii) Solvents used to dryclean clothes are usually chlorinated compounds such as tetrachloroethylene C<sub>2</sub>Cl<sub>4</sub> which is a potential human carcinogen. These materials also have serious environmental consequences.

**Dr. Joe Desimone** has discovered a substitute for chlorinated compounds by synthesising cleaning detergents that work in liquid carbon dioxide. The detergents are such that one end of the molecule is soluble in non-polar substances like grease and oil stains, while the other end dissolves in liquid CO<sub>2</sub>. The breakthrough process is paving the way for designing replacements for conventional halogenated solvents currently used in manufacturing and in industries making coatings.

- (iv) Switching from air (78% nitrogen) to pure oxygen eliminates NO production and also saves fuel by more efficient burning. This has been achieved by glass manufacturers in the U.S.
- (v) Scientists are engineering biodegradability into some synthetic polymers. Certain bonds or groups are introduced into the molecules to make them susceptible to fungal or bacterial attack or to decomposition by moisture. Recently, a biodegradable polymer called Biomax has been developed which decomposes in about eight weeks in a landfill. Biomax could be used in a variety of applications such as lawnbags, bottles, liners of disposable diapers, disposable eating utensils and cups.
- (vi) The current commercial method for producing ibuprofen is a stunning application of green chemistry. Conventional methods of ibuprofen production required six steps, used large amounts of solvents and generated significant quantities of wastes. By using a catalyst that also serves as a solvent, BHC company has discovered a method of ibuprofen production in just three steps with a minimum of solvents and waste.
- (vii) Urea is a major fertilizer used worldwide. It provides nitrogen to soil by decomposing to ammonia and CO<sub>2</sub> when acted on by urease, an enzyme in soils. The ammonia is then taken up by plants.

$$NH_2CONH_2 + H_2O \xrightarrow{Urease} 2NH_3 + CO_2$$

However, the efficiency of urea as a fertilizer is reduced because of 30% ammonia is lost by evaporation before it can be taken up by plant roots. To overcome this loss, a formulation named **Agrotrain** has been developed which acts as urease inhibitor, *i.e.*, this formulation reduces the rate at which urease decomposes urea so that ammonia is released more slowly and efficiently.

## SOME SOLVED PROBLEYS

**Example 1.** Explain the tropospheric pollution in 100 words.

**Solution:** Troposphere is the lowest region of the atmosphere, *i.e.*, closest to the earth. It extends roughly to a height of about 11 km. It contains mainly nitrogen and oxygen. It also contains argon, carbon dioxide, water vapours, aerosols and traces of many other gases. The pollution of troposphere occurs due to the presence of undesirable gases and particulates. The main pollutant gases are:

- (i) Oxides of carbon (CO and CO<sub>2</sub>)—CO is a major pollutant.
- (ii) Oxides of sulphur (SO<sub>2</sub> and SO<sub>3</sub>)
- (iii) Oxides of nitrogen (NO and NO2)
- (iv) Hydrocarbons
- (v) Hydrogen sulphide (H<sub>2</sub>S), etc.

The particulate pollutants include dust, mist, fumes, smoke and aerosols.

**Example 2.** Carbon monoxide is more dangerous than carbon dioxide gas. Why?

**Solution:** Carbon monoxide is highly poisonous in nature. It combines readily with haemoglobin (it has 200 times more affinity than oxygen). Due to the formation of carboxy-haemoglobin, the quantity of oxygen to the body cells gets reduced, *i.e.*, CO reduces the oxygen carrying capacity of the blood and this leads to oxygen starvation (anoxia). The deficiency of oxygen produces headache, dizziness, choking, cardiac and pulmonary complications leading to paralysis and death.

CO<sub>2</sub> does not combine with haemoglobin. However, it is a greenhouse gas and helps in global warming. Hence, it is a less dangerous pollutant.

**Example 3.** Which gases are responsible for greenhouse effect? List some of them.

**Solution:** The gases which are transparent to sunlight and are capable of absorbing IR radiations and then re-emitting IR radiations of longer wavelengths are termed greenhouse gases. Some of these gases are: carbon dioxide; water vapours; oxides of nitrogen; methane; ozone; chlorofluorocarbons.

**Example 4.** Statues and monuments of India are affected by acid rain. How?

or

why is acid rain considered as a threat to Taj Mahal?

**Solution:** Taj Mahal (statues and monuments) is made of marble. The acid rain contains  $H_2SO_4$  which attacks the marble.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

As a result, the monuments (Taj Mahal) are being slowly corroded and the marble is getting discoloured and lustreless.

**Example 5.** What is smog? How are classical and photochemical smogs different?

**Solution:** Smog is a combination of smoke and fog. There are two types of smog:

- (a) Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphur dioxide. Chemically, it is a reducing mixture.
- (b) Photochemical smog occurs in warm, dry and sunny climate. It is formed by the action of sunlight on unsaturated hydrocarbons and nitrogen oxides. Chemically, it is an oxidising mixture. It does not involve any smoke or fog.

**Example 6.** Write down the reactions involved during the formation of photochemical smog.

**Solution :** Sunlight causes photochemical decomposition of NO<sub>2</sub>.

$$NO_2 + h\nu \longrightarrow NO + O$$

Atomic oxygen combines with molecular oxygen to form ozone.

$$O_2 + O + M \longrightarrow O_3 + M$$

*M* is an inert gas such as nitrogen. It takes up the excess energy. Ozone attacks the unsaturated hydrocarbon.

A second process involving hydrocarbons may be depicted as:

$$\begin{array}{c} \mathrm{NO_2} + hv \longrightarrow \mathrm{NO} + \mathrm{O} \\ \mathrm{O} + R\mathrm{H} \longrightarrow R^{\bullet} + R\mathrm{C}\mathring{\mathrm{O}} \\ R\mathrm{C}\mathring{\mathrm{O}} + \mathrm{O_2} \longrightarrow R\mathrm{C}\mathring{\mathrm{O}}_3 \\ R\mathrm{C}\mathring{\mathrm{O}}_3 + \mathrm{NO_2} \longrightarrow R\mathrm{CO}_3\mathrm{NO}_2 \end{array}$$

(peroxyacetyl nitrate, PAN)

The oxidation of hydrocarbons produces various organic intermediates which are less volatile. These substances condense into small droplets of liquid. The dispersion of these droplets in air forms smog. This reduces visibility and looks hazy.

**Example 7.** What are the reactions involved for ozone layer depletion in the atmosphere?

**Solution:** Two types of the compounds have been found responsible for destruction of ozone.

(i) Nitric oxide: Though, nitrous oxide is quite inert in the stratosphere, it is photochemically decomposed into more reactive nitric oxide.

$$N_2O + h\nu \longrightarrow NO + N$$

Nitric oxide, so formed, undergoes the following chain reactions:

$$\begin{array}{c}
NO + O_3 \longrightarrow NO_2 + O_2 \\
O_3 + hv \longrightarrow O_2 + O \\
NO_2 + O \longrightarrow NO + O_2 \\
\hline
2O_3 \longrightarrow 3O_2
\end{array}$$

Net reaction

Thus, in presence of oxides of nitrogen, the rate of decomposition of  $O_3$  increases.

(ii) Chlorofluorocarbons: Chlorofluorocarbons absorb wavelengths between 175 nm and 220 nm and produce chlorine atoms by breaking carbon-chlorine bonds.

$$CF_2Cl_2 + hv \longrightarrow CF_2Cl + Cl$$
  
 $CFCl_3 + hv \longrightarrow CFCl_2 + Cl$ 

Chlorine atoms undergo the following reactions:

$$\begin{array}{c}
\text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{O} \longrightarrow \text{Cl} + \text{O}_2 \\
\hline
\text{O}_3 + \text{O} \stackrel{\text{Cl}}{\longrightarrow} 2\text{O}_2
\end{array}$$

Net reaction

Chlorine atoms catalyse the decomposition of O<sub>3</sub>.

**Example 8.** Answer the following questions:

- (i) What are viable and non-viable particulates?
- (ii) Fish do not grow as well in warm water as in cold water. Why?
  - (iii) What is pneumoconiosis? How does it occur?

**Solution:** (i) Viable particulates are living species such as bacteria, fungi, moulds, algae, etc. These are of small size.

Non-viable particulates are non-living which are formed by disintegration of large size materials or by condensation of small size particles or droplets. The examples are dust, mist, fume, smoke, etc.

- (ii) The amount of dissolved oxygen is less in warm water than cold water.
- (iii) Pneumoconiosis is a disease of lungs. It is caused by small sized particulates which enter into lung through nose and provide a large surface area for adsorption of carcinogenic compounds such as polynuclear hydrocarbons, asbestos, etc.

**Example 9.** What are the major causes of water pollution? Explain.

**Solution:** The main sources responsible for the pollution of water are:

- (a) Sewage and domestic wastes, e.g., human excreta, sewage, sludge, soaps and detergents, domestic wastes, etc.
- (b) **Industrial effluents:** These contain toxic chemicals and hazardous compounds both organic and inorganic.
- (c) Agricultural discharges: These include fertilizers, pesticides, insecticides, herbicides, etc.
- (d) **Thermal discharges:** Used water from power plants and industries is discharged directly into water bodies. The temperature of water bodies thus increases. This brings down DO level which is harmful for aquatic animals.
- (e) Oil: Oil and oil wastes enter rivers and other water bodies. Since oil is insoluble in water, it floats and spreads rapidly into a thin layer. This layer on the surface of water lowers DO level in water.

**Example 10.** (a) What do you mean by biochemical oxygen demand (BOD)?

(b) What is COD? Why is it preferred over BOD?

**Solution:** (a) The micro-organisms which decompose the organic matter present as waste in water need oxygen. The total amount of oxygen consumed by micro-organisms in decomposing the organic waste-present in a certain volume of a sample of water is called biochemical oxygen demand (BOD) of the water.

(b) The amount of oxygen consumed by all the pollutants measured by using a strong oxidising agent generally acidified  $K_2Cr_2O_7$  and expressed in ppm is called COD (chemical oxygen demand) of the given sample of water.

COD is preferred over BOD because the measurement of BOD takes a number of days (about 5 days) whereas COD can be determined in a very short time.

**Example 11.** (i) What would have happened if the greenhouse gases were totally missing in the earth's atmosphere? Discuss.

- (ii) What do you mean by green chemistry?
- (iii) How can domestic waste be used as manure?
- (iv) What are pesticides?
- (v) Explain the term "Eutrophication".

**Solution:** (i) The solar energy radiated back from the earth surface is absorbed by greenhouse gases which re-emit IR radiations or longer wavelengths. These radiations heat up the atmosphere near the earth's surface and keep it warm. If there were no greenhouse gases, the earth would be a very cold place and there would have no vegetation and life on earth.

- (ii) Green chemistry practices producing the chemicals of our daily use employing such reactions and chemical process which neither use toxic chemicals nor emit toxic chemicals into the atmosphere. This is the one way to protect our environment from chemical wastes.
- (iii) Domestic waste consists of two types of wastes, biodegradable and non-biodegradable. The biodegradable waste is separated and deposited in the landfills. With a passage of time, it is converted into manure consisting nitrogen and phosphorus compounds by micro-organisms.
- (iv) These are synthetic toxic chemical substances which are used in agriculture to control the damages done by insects, rodents, weeds and various crop diseases. The repeated use produces resistance in the pests and thus new substances are to be discovered in due course of time. DDT, BHC, aldrin and dieldrin have been tried as insectides. Now-a-days, organophosphates and carbamates have been in use as insectides.
- (v) The presence of excessive nutrients in a lake due to inflow of nutrients from fertilizers results in the increase of phosphate ions in water. As a result, the formation of algae is accelerated and the concentration of dissolved oxygen decreases. This process is called eutrophication. This badly affects the aquatic life.

## -•••- PRACTICE PROBLEMS -•••-

### ■ Subjective Type Questions

- 1. Name the four distinct regions of atmosphere.
- 2. Name the non-living components of environment.
- **3.** Name the zone of the atmosphere where ozone layer is present.
- 4. Name three greenhouse gases.
- 5. Define the term biosphere.
- **6.** What are the principal chemical species present in the stratosphere?
- 7. What is the wavelength range of the ultraviolet radiation which is removed in the stratosphere?
- 8. What is pollution?
- 9. What are pollutants?
- 10. What are primary pollutants? Give three examples.
- 11. What are secondary pollutants? Give three examples.
- 12. Name the main sources of air pollutants.
- 13. Name the two major man-made sources of oxides of nitrogen to the atmosphere.
- 14. Which oxide of nitrogen is a major concern as an air pollutant?
- 15. Which is the largest air pollutant in urban atmosphere?
- 16. Define photochemical oxidant.
- 17. Name two photochemical oxidants.
- 18. What is particulate?
- 19. Name four effects of air pollution.
- 20. What is acid rain?
- 21. Why is normal rain slightly acidic?
- 22. Name the two strong acids present in the acid rain.
- 23. What primary pollutants are responsible for photochemical smog?
- 24. Define greenhouse gases.
- 25. Select the gases which can absorb IR-radiation:
  Oxygen, carbon dioxide, methane, nitrogen, chlorofluorocarbons
- **26.** In the absence of greenhouse effect, what would be the mean temperature of the earth?
- 27. Define radiative forcing.
- **28.** What is the relative contribution of carbon dioxide to the greenhouse effect?
- 29. Suggest three ways to reduce greenhouse effect.
- **30.** Which substances are considered as responsible for the depletion of ozone layer?
- **31.** Name the regions of the atmosphere where global warming and ozone depletion phenomenon occur.
- 32. Define water pollution.
- 33. Name five common water pollutants.
- 34. Define green chemistry.
- 35. Give three suggestions for minimising pollution.
- **36.** Which of the following is more effective greenhouse gas: CO or H<sub>2</sub>O?

- 37. Which of the following gases qualify as greenhouse gases? CO, NO, NO<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub>, Ne.
- 38. Which gas leaked to bring havoc in Bhopal tragedy?
- **39.** What is the compound formed when CO combines with haemoglobin?
- 40. What is anoxia?
- **41.** How are the flue gases from industries freed from oxides of nitrogen and sulphur?
- 42. What are asbestosis and silicosis?
- **43.** What is the composition of London smog?
- 44. What is the nature of classical smog?
- **45.** In which season and what time of the day, there is photochemical smog?
- **46.** Name two important sinks of CO<sub>2</sub>.
- **47.** What is humification?
- 48. Define pollution. Give its main causes.
- 49. What are the different air pollutants? Give their main sources.
- 50. Describe troposphere briefly.
- 51. Describe stratosphere briefly.
- Describe in short the various non-living components of environment.
- 53. Describe the main effects of air pollution.
- 54. How can air pollution be controlled?
- 55. Give the chemistry of acid rain. What are its effects?
- **56.** How has the ozone layer been affected by the oxides of nitrogen?
- **57.** Discuss in short the chemistry of the formation of photochemical smog.
- **58.** What is greenhouse effect? Which atmospheric gases are responsible for this effect?
- **59.** Write a short note on global warming:
  - (i) Name two common air pollutants.
  - (ii) Name two important sources of these pollutants.
  - (iii) Name one gas which causes greenhouse effect. What are the harmful consequences of this effect?

[I.S.C. 2000]

- **60.** Growth in human population has direct effect on pollution. Explain.
- **61.** Can pollution of the environment occur without human intervention? Explain.
- 62. Discuss water pollution. How can it be controlled?
- 63. Explain the main effects of water pollution.
- **64.** How does excessive use of pesticides and fertilizers in agriculture pollute our biosphere?
- **65.** What suggestions would you like to give to minimise pollution?
- **66.** How has the ozone layer been affected by the use of chlorofluorocarbons? What steps have been proposed to save the ozone layer?
- 67. Give three ways to prevent soil pollution.
- **68.** Define green chemistry. What are its objectives?

- **69.** Compare global warming phenomenon with ozone depletion phenomenon.
- **70.** Which one, carbon dioxide or carbon monoxide, is more toxic to human beings? Why?
- **71.** What are the harmful effects of photochemical smog and how can they be controlled?
- 72. What do you mean about ozone hole? What are its consequences?
- 73. A large number of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.

[Hint: Quantity of dissolved oxygen decreases in water.]

- 74. Write short notes on the following:
  - (i) Primary and secondary pollutants
  - (ii) Biodegradable and non-biodegradable pollutants
  - (iii) Contaminant
- 75. How ozone layer is formed and acting as a protecting umbrella?
- **76.** Discuss the importance of dissolved oxygen in water. How is COD of a polluted water measured?
- 77. Name at least four soil pollutants. Explain one of them.
- 78. What are pesticides and herbicides? Explain giving examples.
- **79.** How should the management of domestic and industrial wastes be done?
- **80.** Define atmosphere. Give an account of the composition and structure of atmosphere.
- **81.** Define pollution. Give an account of environmental pollutants. Describe their sources and suggest suitable methods of control of air pollution.

- **82.** Is ozone useful or harmful to us? Discuss the chemistry of ozone depletion. Discuss also the threats to its depletion in atmosphere.
- 83. Write an essay on photochemical smog.
- 84. Write an essay on greenhouse effect and global warming.
- 85. What are the major sources of water pollution? Discuss the nature of the pollutants involved and suggest methods of control.
- 86. Write an essay on green chemistry.
- **87.** Do you observe any soil pollution in your neighbourhood? What efforts will you make for controlling the soil pollution?
- **88.** What do you mean by green chemistry? How it will help in decreasing environmental pollution?
- 89. What are international standards for drinking water?
- **90.** Explain the strategies which should be adopted to control environmental pollution.
- **91.** What do you understand by BOD and COD? How are these determined? Which one is preferred?

#### Matching Type Questions

#### Match the Column-I with Column-II:

	Column-I		Column-II
(a)	Greenhouse effect	(p)	Primary pollutant
(b)	Smoke	(q)	Non-Biodegradable
(c)	Nitric oxide	(r)	Photochemical oxidant
(d)	PAN	(s)	Bone disease
(e)	Fluorosis	(t)	Physical pollutant
(f)	Noise	(u)	Chlorofluorocarbons
(g)	Plastic	(v)	Global warming
(h)	Ozone depletion	. (w)	Particulate

### Answers

#### Answers: Subjective Type Questions

- 1. (a) Troposphere (b) Stratosphere (c) Mesosphere
  - (d) Thermosphere.
- 2. (a) Atmosphere (b) Hydrosphere (c) Lithosphere
- 3. Stratosphere
- 4. (i) Carbon dioxide (ii) water vapours (iii) nitrous oxide.
- The environment which supports life. It extends to about 20 km from the bottom of the ocean to the highest point in the atmosphere at which life can survive.
- 6.  $O_3$ ,  $O_2$ ,  $N_2$ , and some water vapours.
- Ultraviolet radiations between 190 to 340 nm are removed in the stratosphere.
- 8. Any undesirable change in the physical, chemical and biological characteristics of air, water and land which is harmful to man directly or indirectly is termed pollution.
- Pollutants are chemical, biological or physical agents that exert undesirable effects on living organisms including human health, environment or belongings.
- Primary pollutants are those which are emitted directly from the sources. The examples are: particulate matter, carbon monoxide, sulphur dioxide, nitric oxide, etc.
- 11. Secondary pollutants are those which are formed in the atmosphere by chemical interactions among primary pollutants and normal atmospheric constituents. The examples are: sulphur trioxide, nitrogen dioxide, PAN and PBN, etc.
- 12. (i) Combustion of fossil fuels such as coal, petroleum and natural gas.
  - (ii) Industrial processes
- (iii) Agricultural burning
- 13. (i) Fossil fuel based power plants (ii) Automobiles.
- **14.** Nitrogen dioxide **15.** Carbon monoxide
- 16. Photochemical oxidant is an atmospheric substance which is produced by a photochemical process which can oxidise materials not readily oxidised by oxygen. These are secondary pollutants.
- 17. Ozone, peroxy-acetyl nitrate.
- 18. Particulate refers to any atmospheric substance which is not in gaseous state. It can be a solid or a liquid or a mixture of the two.
- 19. (i) Harmful effects on human health
  - (ii) Harmful effects on vegetation
  - (iii) Damage to materials
- (iv) Climatic changes.

- **20.** It describes all precipitation-rain, snow, fog, dew-which is more acidic than normal rain, *i.e.*, pH is less than 5.6.
- 21. CO<sub>2</sub> on dissolution produces a weak carbonic acid.
- 22. Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and nitric acid (HNO<sub>3</sub>).
- 23. Nitric oxide, carbon monoxide and various unburned hydrocarbons are the primary pollutants which are responsible for the formation of photochemical smog in presence of sunlight.
- 24. The gases which are transparent to sunlight and are capable of absorbing IR-radiation and then to re-emit IR-radiation of longer wavelengths are termed greenhouse gases.
- 25. Carbon dioxide, methane, chlorofluorocarbons.
- **26.** − 15°C
- **27.** The amount of warming which a greenhouse gas imparts to 1 square metre of the earth is called radiative forcing.
- **28.** 50%.
- 29. (i) Non-fossil energy sources should be adopted (ii) The production and use of chlorofluorocarbons should be banned (iii) Deforestation should be prevented (iv) Population of the world must be stabilised.
- 30. (i) Oxides of nitrogen (ii) Chlorofluorocarbons.
- 31. Global warming-Troposphere: Ozone depletion-Stratosphere.
- 32. See text
- (i) Oxygen demanding wastes (ii) Synthetic organic compounds (iii)
   Inorganic Chemistry and minerals (iv) Fertilizers (v) Sewage.
- 34. See text 35. See text
- **36.** H<sub>2</sub>O **37.** CO, NO and NO<sub>2</sub>
- 38. Methyl isocyanate
- 39. Carboxyhaemoglobin
- 40. Acute oxygen starvation in the body.
- By passing through alkaline solutions of Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> or through conc. H<sub>2</sub>SO<sub>4</sub>.
- **42.** The lung disease caused by particulates of asbestos and silica respectively.
- 43. Fog of H<sub>2</sub>SO<sub>4</sub> droplets deposited on carbon particulates.
- 44. Reducing 45. Summer, daytime (after noon)
- 46. Ocean, plants (photosynthesis)
- The decomposition of organic matter in the soil by micro-organisms to produce humus.

Answers: Matching Type Questions

(a-v); (b-w); (c-p); (d-r); (e-s); (f-t); (g-q); (h-u)

## **OBJECTIVE QUESTIONS**



**Set I**: This set contains questions with single correct answer.

1.	Biosphere includes:		12.	Which one is not a water pollutant?	
	(a) Hydrosphere only $\Box$ (b) lithosphere only $\Box$	]		(a) Automobile exhaust	
		]		(b) Plant nutrients	
2.	Which one is not the correct statement?			(c) Oxygen demanding wastes	
	Pollution means:			(d) Disease causing agents	
	(a) the presence of anything in the environment in excess	ss	13.	Lung diseases are four times more in urban areas than re	aral
	or mo required minu	]		areas. This is due to the presence of:	
	(b) anything put into the environment which was not ther	e	•	(a) $SO_2$	
		]		(c) $N_2$	
	(c) direct or indirect changes in one or more components of		14.	The loss or reduction of chlorophyll in the leaves is term	ied:
	the ecosystem which are not harmful to living organism	ıs		(a) necrosis	
		]		(c) epinasty	
	(d) international release of any chemical substance in the	_ 1	15.	Which statement is not correct?	_
_		]		(a) CO is the main air pollutant	
3.	Which one is not a chemical pollutant?	_		(b) All pollutants are not wastes	
		]		(c) Water is polluted by dissolved oxygen	
	(-)	ן כ		(d) Lichens are pollution indicators	
4.	Which is the main air pollutant?	_	16.	Which one is not correct?	
	(-)	<b>-</b>		Greenhouse effect:	
_	(c) $N_2$			(a) is due to high concentration of CO <sub>2</sub> in atmosphere	
5.	Which is not an air pollutant?	<b>-</b>		(b) is influenced by gases such as CH <sub>4</sub> , O <sub>3</sub> and chlo	
	· · · · · · · · · · · · · · · · · · ·	3		fluorocarbons	
6	(7)	-		(c) would result in the warming up of the earth	_
6.	Which one is the bio-degradable pollutant?  (a) Lead compounds	ם		(d) would result in lowering the level of oceans due to he	ngn
		<u>-</u>	17.	evaporation Which one is not a correct statement? To minimise pollut	
7.	Which one is not a correct statement?	<b>-</b>	1/.	(a) manures and biofertilizers should be used in place	
<i>,</i> .	(a) Primary pollutants are those which are emitted direct	lv		chemical fertilizers	
	from the source	7		(b) all nuclear tests must be stopped	
	(b) Secondary pollutants are those which are formed in the	ne		(c) green belts in cities should be developed	
	atmosphere by chemical interactions among primar			(d) domestic garbage must be burnt	
		i l	18.	Which is the most harmful for life on the globe?	
				(a) Deforestation	
	(d) Particulates refer to all atmospheric substances that a	re		(c) Increasing desert	
			19.	If BOD of river is high, it means that the river is:	
8.	Which one of the following is an invaluable source of energy	gy		(a) not polluted	
	but does not cause pollution?			(b) very much polluted with inorganic chemicals	
	(a) Petroleum			(c) very much polluted with organic chemicals which	are
				decomposed by micro-organisms	
9.	The acid rain possesses:			(d) polluted with pesticides	
			20.	Which of the following is produced by reaction of ultravi	olet
	( ) I	╸╽		light?	
10.	All except which cause pollution:			(a) CO $\square$ (b) SO <sub>2</sub>	
				(c) $O_3$	
	(-)		21.	Earth is protected from UV-radiations by:	_
11.	DDT is:	_		(a) ozone layer	
			22	(c) carbon dioxide	
			22.	Which air pollutant is not released by scooters and car	
	• •			(a) SO <sub>2</sub>	
	(d) dichlorodifluorotitanium			(c) Hydrocarbons	

23.	Photo-chemical oxidants such as PAN or PBN are formed:	35.	Ozone hole refers to:	
	(a) by action or nitrogen oxides on hydrocarbons in		(a) increased concentration of ozone	
	presence of sunlight	.	(b) reduction in the thickness of ozone layer in troposphere	
	(b) by action of carbon dioxide on hydrocarbons in			
	presence of sunlight	1	(c) reduction in the thickness of ozone layer in stratosphere	
	(c) by action of hydrogen sulphide on hydrocarbons in			
	presence of sunlight	İ	(d) hole in ozone layer	
	(d) none of these	36.		
24.		30.	of water over a period of time is done to find out:	
4 <b>4.</b>				
	(a) pesticides in water		(a) biogas generation	
	(b) fluorides in water		(b) biological oxygen demand	
	(c) carbon monoxide in air		(c) biosynthetic pathways	
	(d) sulphur dioxide in air	25	(d) fermentation	
25.	The pollutants released by jet aeroplanes in the atmosphere	37.	One of the metals used as a catalyst in automobiles' catalytic	
	as fluorocarbons are called:		converter is:	
	(a) photochemical oxidants		(a) palladium	
	(b) photochemical reductants	20	(c) radium	
	(c) aerosols	38.	Photochemical smog is related to the pollution of:	
	(d) physical pollutants		(a) soil	
26.	Pollution can be controlled by:	20.	(c) noise $\Box$ (d) air $\Box$	J
	(a) sewage treatment	39.	Lead is considered as:	
	(b) manufacturing electrically operated vehicles		(a) water pollutant	
	(c) adopting green chemistry	100	(c) air pollutant	J
	(d) all of the above	40.	Gas released during Bhopal tragedy was:	. 1
27.	The chief pollutants which are responsible for ozone		(a) sodium isothiocyanate	
	depletion:		(b) ethyl isothiocyanate	_
	(a) $SO_2$		(c) potassium isothiocyanate	
	(b) CO <sub>2</sub>		(d) methyl isothiocyanate	•
	(c) CO	41.	Pollutant is a chemical substance or factor which disturbs:	
	(d) oxides of nitrogen and chlorofluorocarbons		(a) our balanced environment	
28.	SO <sub>2</sub> and NO <sub>2</sub> cause pollution by increasing:	į	(b) geochemical cycles	
	(a) acidity	1.0	(c) flora of any region □ (d) fauna of any region □	i
••	(c) buffer action $\Box$ (d) none of these $\Box$	42.	A brick kiln should not be allowed near an orchard:	
29.	Taj Mahal is threatened due to effect of:		(a) to save plants from soil erosion	
	(a) chlorine	1	(b) to save fruits from labourers	
20	(c) oxygen		(c) to save plants from smoke and toxic gases emitted by	,
30.	Catalytic converter in automobiles is used to control:		kiln	! •
	(a) water pollution		(d) to save plants from transport vehicles	_
21	(c) air pollution	43.	The basic component of smog is: [A.M.U. (Med.) 2005]	-
31.	Most important cause of soil pollution is:		(a) PAN	
	(a) iron junks		(c) NO <sub>2</sub>	
22	(c) detergents		In Antarctica, ozone depletion is due to the formation of the	
32.			following compounds: [P.E.T. (Kerala) 2005	_
	will:		(a) acrolin	_
	(a) increase	i	(c) SO <sub>2</sub> and SO <sub>3</sub>	
áa	(c) decrease	45.	An object is located at a height of 5 km from the surface of	
33.	Which of the following is the secondary pollutant?		the earth. The object is located in which part of the	
	(a) CO	1	atmosphere? [E.A.M.C.E.T. (Med.) 2006	_
24	(c) SO <sub>2</sub>		(a) Thermosphere	_
<i>3</i> 4.	If there was no carbon dioxide in earth's atmosphere, the		(c) Stratosphere	
	temperature of the earth's surface would be:		CFCl <sub>3</sub> is responsible for the decomposition of ozone to form	
	(a) same as present		oxygen. Which of the following reacts with ozone to form	
	(b) less than the present	. 1	oxygen? [E.A.M.C.E.T. (Engg.) 2006	-] T
	(c) more than the present	'		1
	(d) dependent on the amount of oxygen in the atmosphere	-	(c) $F^-$	ı

47	The photochemical smog can be suppressed by:	51	In which part of atmosphere, ozone layer is present?
₹/•	[P.E.T. (Kerala) 2007]	31.	[D.C.E. 2008]
	(a) nitrogen oxides $\Box$ (b) hydrocarbons $\Box$		(a) Stratosphere
	(c) radical traps		(c) Mesosphere
	(e) peroxyacetyl nitrate	52.	Which of the following is secondary pollutant?
48.	Which of the following is not an air pollutant?		[D.P.M.T. 2008]
	[E.A.M.C.E.T. (Med.) 2007]		(a) $CO_2$ $\square$ (b) $N_2O$ $\square$
	(a) CO $\square$ (b) SO <sub>2</sub> $\square$		(c) PAN $\square$ (d) $SO_2$ $\square$
	(c) NO $\square$ (d) $N_2$ $\square$	53.	Among the following compounds, which one is not
49.	Green chemistry means such reactions which:		responsible for depletion of ozone layer?
	[C.B.S.E. 2008]		[E.A.M.C.E.T. (Engg.) 2008]
	(a) are related to the depletion of ozone layer $\Box$		(a) $CH_4$
	(b) produce colour during reactions		(c) NO $\square$ (d) $\operatorname{Cl}_2$ $\square$
	(c) study the reactions in plants $\square$	54.	
	(d) reduce the use and production of hazardous chemicals		equilibrium between O <sub>2</sub> and CO <sub>2</sub> in atmosphere?
<b>=</b> 0			[E.A.M.C.E.T. (Med.) 2008]
50.	Identify the wrong statement in the following:		(a) Chlorophyll $\square$ (b) Vitamin- $B_{12}$ $\square$
	[A.I.E.E.E. 2008]		(c) Porphyrin
	(a) acid rain is mostly because of oxides of nitrogen and	55.	
	sulphur		[P.M.T. (Kerala) 2010]
	(b) chlorofluorocarbons are responsible for ozone layer depletion	İ	(a) SO <sub>2</sub> and NO <sub>2</sub> □ (b) SO <sub>2</sub> and hydrocarbons □
	(c) greenhouse effect is responsible for global warming		(c) NO <sub>2</sub> and hydrocarbons
	(d) ozone layer does not permit infrared radiation from the		(d) O <sub>3</sub> and PAN
	sun to reach the earth		(a) 03 and 1711
Set	II: This set contains questions with two or more cor	rectai	newere
	•		
56.	The gases which are responsible for photochemical smog are:	61.	If the greenhouse effect or global warming remains
	(a) oxides of nitrogen		unchecked, it alter:
e=	(c) carbon monoxide  (d) inert gases		(a) sea levels
5/.	The gases which are responsible for acid rain:	(2)	(c) rainfall
	(a) oxides of nitrogen ☐ (b) oxides of sulphur ☐ (c) hydrocarbons ☐ (d) carbon monoxide ☐	04.	The following reactions occur in the stratosphere: (a) $O_2 + UV \longrightarrow O + O$
59	The gases which are absorbers of IR-radiation:		(a) $O_2 + O \longrightarrow O_3$
56.	(a) oxygen		(b) $O_2 + O \longrightarrow O_3$ (c) $Cl + O_3 \longrightarrow ClO + O_2$
	(c) carbon dioxide		(d) $SO_3 + H_2O \longrightarrow H_2SO_4$
59.	Particulates are added to the atmosphere by:	63	Pollution can be controlled if:
	(a) industrial processes $\square$ (b) combustion of fuels $\square$	00.	(a) all automobiles must be fitted with exhaust system's
	(c) agriculture burning $\square$ (d) photosynthesis $\square$		catalytic converters
60.	The following processes occur in the troposphere:		(b) use of fossil fuels must be minimised and non-
	(a) photosynthesis		conventional energy sources should be developed
	(c) greenhouse effect $\square$ (d) acid rain $\square$		(c) emphasis on green chemistry is given
		1 .	(d) population is stabilised
_			
П	Auswers		
-	/ tweater	· · · · · · · · · · · · · · · · · · ·	
	1. (d) 2. (c) 3. (a) 4. (b) 5. (a)	6	6. (d) 7. (c) 8. (b) 9. (d) 10. (b)
	11. (c) 12. (a) 13. (a) 14. (b) 15. (c)	16	<b>5.</b> (d) <b>17.</b> (d) <b>18.</b> (d) <b>19.</b> (c) <b>20.</b> (c)
	21. (a) 22. (b) 23. (a) 24. (b) 25. (c)		5. (d) 27. (d) 28. (a) 29. (b) 30. (c)
	· · · · · · · · · · · · · · · · · · ·		
	31. (d) 32. (a) 33. (b) 34. (b) 35. (c)		6. (b) 37. (a) 38. (d) 39. (a) 40. (d)
	<b>41.</b> (a) <b>42.</b> (c) <b>43.</b> (a) <b>44.</b> (d) <b>45.</b> (d)	46	6. (d) 47. (c) 48. (d) 49. (d) 50. (d)
	<b>51.</b> (a) <b>52.</b> (c) <b>53.</b> (a) <b>54.</b> (a) <b>55.</b> (d)	56	6. (a,b,c) 57. (a,b) 58. (c,d) 59. (a,b,c)
	<b>60.</b> (a,b,c,d) <b>61.</b> (a,c,d) <b>62.</b> (a,b,c) <b>63.</b> (a,b,c,d)		



## **Objective Questions for IIT ASPIRANTS**



- 1. Fluoride pollution mainly affects:
  - (a) teeth

(b) heart

(c) brain

- (d) kidney
- 2. In 1984, the Bhopal gas tragedy took place because methyl isocyanate:
  - (a) reacted with water
- (b) reacted with DDT
- (c) reacted with ammonia
- (d) reacted with CO<sub>2</sub>
- Maximum permissible limit of noise as per the noise pollution rules 2000 of India is:
  - (a) 75 decibel
- (b) 65 decibel
- (c) 55 decibel
- (d) 50 decibel
- Silicosis is caused by:
  - (a) acid rain
- (b) depletion of ozone
- (c) inhalation of aerosols
- (d) inhalation of sulphur dioxide
- Sterility is caused by which pollutant in water?
  - (a) copper
- (b) mercury.
- (c) cadmium
- (d) manganese
- The pH of acid rain water is:
  - (a) 1.2

(b) 3.1

(c) 5

- (d) 6
- Byssinosis; a disease is caused by:
  - (a) fly ash
- (b) cement dust
- (c) cotton fibres
- (d) lead particles
- 8. Major source of methane in India is:
  - (a) fruit orchards
- (b) sugar cane plantation
- (c) rice fields
- (d) wheat fields
- Which element is believed to be responsible for the fall of the Roman Empire?
  - (a) copper
- (b) lead
- (c) arsenic
- (d) zinc
- 10. Supersonic jets cause pollution by thinning of:
  - (a) CO<sub>2</sub> layer
- (b) SO<sub>2</sub> layer
- (c) O<sub>2</sub> layer
- (d) O<sub>3</sub> layer

- 11. Cracking of rubber is caused due to:
  - (a) acid rain
- (b) soot

(c) smog

- (d) all of these
- 12. Sulphur dioxide affects:
  - (a) cell wall
- (b) brain

(c) skin

(d) membrane system

- **13.** DDT is:
  - (a) greenhouse gas
- (b) degradable pollutant
- (c) non degradable pollutant (d) none of these
- 14. Ultraviolet radiations from sunlight causes a reaction that produces:
  - (a) fluorides
- (b) carbon monoxide
- (c) sulphur dioxide
- (d) ozone
- 15. Newspaper contains a toxic material called:
  - (a) cadmium
- (b) lead
- (c) manganese
- (d) mercury
- 16. Most atmospheric pollutants do not rise above:
  - (a) 6000 m
- (b) 600 m

(c) 60 km

- (d) 6 m
- 17. Jet aeroplanes release the pollutants in air called:
  - (a) smog

- (b) photochemical oxidants
- (c) aerosols
- (d) fly ash
- 18. Non-ionising radiations with specific biological effects are:
  - (a) UV radiations
- (b) Beta rays
- (c) Gamma rays
- (d) X-rays
- 19. Which of the following pollutants is not harmful to the lungs?
  - (a) CO

(b) SO<sub>2</sub>

- (d)  $NO_2$
- 20. Which of the following vehicular fuels is currently accepted as ecofriendly?
  - (a) Diesel

(b) Petrol

(c) LPG

(d) CNG

### tuswers

- 2. (a)
- **1.** (a) 13. (c)
- 14. (d)
- 3. (a) 15. (b)
- 4. (c)
- 16. (b)
- 5. (d) 17. (c)
- **6.** (b) 18. (a)
- 7. (c) 19. (c)
- 8. (c) 9. (b)

20. (d)

- **10.** (d)
- 11. (c)
- 12. (d)

## Assertion-Reason Type Questions

In each of the following questions two statements are given as Assertion (A) and Reason (R). Mark the answer according to following instructions:

- (a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are correct and (R) is not the correct explanation of (A).
- (c) If (A) is correct but (R) is wrong.

- (d) If both (A) and (R) are wrong.
- 1. (A) DDT and BHC are non-biodegradable soil pollutants.
  - (R) DDT and BHC are fertilizers.
- 2. (A) PAN is main constituent of photochemical smog.
  - (R) It is formed by the action of oxides of nitrogen and hydrocarbons in presence of sunlight.
- 3. (A) Earth is protected from IR radiations by ozone layer.
  - (R) Ozone layer is present in troposphere of the atmosphere.

- **4.** (A) CO is a toxic air pollutant.
  - (R) CO binds with haemoglobin of blood and reduces oxygen transport efficiency of blood.
- 5. (A) Photochemical smog is produced by oxides of nitrogen.
- (R) Automobiles are a major source of oxides of nitrogen.
- 6. (A) For greenhouse effect, presence of green plants is essential.
  - (R) Greenhouse effect is responsible for global warming.

### uswers

1. (c)

2. (a)

3. (d)

4. (a)

5. (b)

6. (c)

## THOUGHT TYPE QUESTIONS

#### THOUGHT 1

Nitric oxide (NO) is the nucleus of photochemical smog.

$$2NO(g) + O_2(air) \longrightarrow 2NO_2(g)$$

$$\begin{array}{c}
\text{NO}_2(g) \xrightarrow{\text{Sunlight}} & \text{NO}(g) + [O] \\
[O] + O_2(g) & \longrightarrow & O_3(g)
\end{array}$$

Both NO<sub>2</sub> and O<sub>3</sub> are strong oxidising agents and react with unburnt hydrocarbons in the polluted air to produce formaldehyde, acrolein and peroxyacetyl nitrate (PAN). These products are harmful to the plant and animal life.

Catalytic converters are now installed in the automobiles to reduce the photochemical smog. Photochemical smog can also be suppressed by certain compounds, which act as free radical trap.

- 1. Which are the primary constituents of photochemical smog?
  - (a) SO<sub>2</sub> and CO
- (b) NO<sub>2</sub> and hydrocarbons
- (c) CO<sub>2</sub> and NO<sub>2</sub>
- (d) Hydrocarbons and CFCs
- Photochemical transformation of the automobile exhaust emission in UV wavelength of sunlight results into:
  - (a)  $CH_4$  and  $C_6H_6$
- (b) O<sub>3</sub> and PAN
- (c) CO<sub>2</sub> and NO<sub>2</sub>
- (d) CO and CO2
- Smog is common pollutant in places having:
  - (a) high temperature
  - (b) low temperature
  - (c) excessive ammonia in the air
  - (d) excessive sulphur dioxide in the air
- 4. Photochemical smog formed in congested metropolitan cities mainly consist of:
  - (a) hydrocarbons, SO2 and CO2
  - (b) hydrocarbons, ozone and SO<sub>2</sub>
  - (c) ozone, peroxyacetyl nitrate and NO<sub>r</sub>
  - (d) smoke, peroxyacetyl nitrate and SO<sub>2</sub>

#### THOUGHT 2

Ozone layer acts as one of the most important life support system. The major cause of ozone layer destruction is believed to be the release of chlorofluorocarbon compounds. UV radiation causes the chlorofluorocarbons to dissociate:

$$CF_2Cl_2 \xrightarrow{h\nu} Cl^* + \overset{*}{C}F_2Cl$$

A highly reactive chlorine atom is responsible for the decomposition of ozone.

$$Cl^* + O_3 \longrightarrow ClO^* + O_2(g)$$
  
 $ClO^* + O(g) \longrightarrow Cl^* + O_2(g)$ 

Free radicals of chlorine decompose ozone molecules in a chain reaction. The depletion of ozone layer leading to ozone hole has, however, been mainly observed in the stratosphere over Antarctica. Special type of cloud called polar stratospheric clouds are formed over Antarctica. These clouds (contain solid HNO<sub>3</sub>·3H<sub>2</sub>O) play an important role in ozone depletion.

$$CIO^* + NO_2 \longrightarrow CIONO_2$$
  
 $CIONO_2 + H_2O \longrightarrow HOCl + HNO_3$   
 $CIONO_2 + HCl \longrightarrow Cl_2 + HNO_3$ 

$$HOCl \xrightarrow{h\nu} HO^* + Cl^*$$

The reactive chlorine atoms thus formed are rendered to deplete ozone layer.

- 1. The ozone layer is present in:
  - (a) troposphere
- (b) stratosphere
- (c) mesosphere
- (d) thermosphere
- The result of ozone hole is:
  - (a) acid rain
- (b) greenhouse effect
- (c) global warming
- (d) the UV radiation reach to earth
- 3. Freon is not recommended to be used in refrigerators because thev:
  - (a) increase temperature
- (b) deplete ozone
- (c) affect environment
- (d) affect human body
- Ozone in stratosphere is depleted by:
- [A.I.I.M.S. 2004]
- (a)  $C_6F_6$ (b)  $C_7F_{16}$ 
  - (c) CF<sub>2</sub>Cl<sub>2</sub> (d)  $C_6H_6Cl_6$
- 5. Peeling of ozone umbrella, which protects us from UV rays is caused by:
  - (a) PAN
- (b) CO<sub>2</sub>
- (c) CFCs
- (d) coal burning

Thought 1 1. (b) Thought 2

- **1.** (b)
- 2. (b) 2. (d)
- **3.** (a) 3. (b)

- 4. (c) **4.** (c)
- 5. (c)



## MISCELLANEOUS .......

#### TYPE 1: Short and Very Short Questions

#### ACTION OF HEAT ON COMPOUNDS

- Q. 1. What happens when the following nitrates are heated?
  - (a) NaNO<sub>3</sub> (Chile saltpetre)
  - (b) KNO<sub>3</sub> (Nitre)
  - (c) AgNO<sub>3</sub> (Lunar caustic)
  - (d) Hg(NO<sub>3</sub>)<sub>2</sub> (Mercuric nitrate)
  - (e) NH<sub>4</sub>NO<sub>3</sub>

(d)

- (f) Nitrates of heavy metals like Cu, Zn, Pb, Ca and Ba.
- (g) LiNO<sub>3</sub> (Lithium nitrate) and Mg(NO<sub>3</sub>)<sub>2</sub> (magnesium nitrate).
- Ans. (a) At 316°C, it melts and decomposes to nitrite and oxygen on further heating.

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

(b) KNO<sub>3</sub> melts at 336°C and decomposes like NaNO<sub>3</sub> on further heating.

$$2KNO_3 \longrightarrow 2KNO_2 + O_2$$

(c) Lunar caustic melts at 209°C. It decomposes on further heating according to the following chemical reactions:

$$2AgNO_3 \longrightarrow 2AgNO_2 + O_2$$
  
 $2AgNO_2 \longrightarrow 2Ag + 2NO_2$ 

- $Hg(NO_3)_2 \longrightarrow Hg + 2NO_2 + O_2$
- (e) NH<sub>4</sub>NO<sub>3</sub> melts at 165°C and decomposes at 200°C to give laughing gas. Above 260°C its reaction becomes explosive.

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

(f) Heavy metal nitrates decompose to give metal oxide along with  $NO_2$  and  $O_2$ .

$$2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$$

$$2Ba(NO_3)_2 \xrightarrow{\Delta} 2BaO + 4NO_2 + O_2$$

$$2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2$$

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$$

(g) Nitrates of lithium and magnesium decompose on heating giving mixture of nitrogen dioxide and oxygen.

$$4\text{LinO}_3 \longrightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$$
  
 $2\text{Mg(NO}_3)_2 \longrightarrow 2\text{MgO} + 4\text{NO}_2 + \text{O}_2$ 

- Q. 2. What happens when the following carbonates are heated?
  - (a) Washing soda (Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O)
  - (b) Silver and mercury carbonate (Ag<sub>2</sub>CO<sub>3</sub>, Hg<sub>2</sub>CO<sub>3</sub>)
  - (c) Ammonium carbonate [(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>]
  - (d) Limestone (CaCO<sub>3</sub>)
  - (e) Basic copper carbonate [CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>]
  - (f) Zinc carbonate (ZnCO<sub>3</sub>).
- Ans. (a) Dehydration takes place on heating the washing soda.

$$Na_2CO_3 \cdot 10H_2O \xrightarrow{\Delta} Na_2CO_3 \cdot H_2O$$
 (melts at 950°C)  
 $Na_2CO_3 \cdot H_2O \xrightarrow{\Delta} Na_2CO_3$  (anhydrous)

(b) Silver and mercury carbonates decompose on heating to corresponding metal.

$$\begin{array}{ccc}
2Ag_2CO_3 & \xrightarrow{\Delta} & 4Ag + 2CO_2 + O_2 \\
2Hg_2CO_3 & \xrightarrow{\Delta} & 4Hg + 2CO_2 + O_2
\end{array}$$

(c) Ammonium carbonate on heating changes to ammonium bicarbonate followed by ammonium carbamate.

$$2(NH_4)_2CO_3 \longrightarrow NH_4HCO_3 + NH_2COONH_4$$

carbamate

+ H<sub>2</sub>O + NH<sub>3</sub>

(d) Limestone decomposes on heating to evolve CO<sub>2</sub> gas, leaving behind CaO.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

(e) Carbonate of copper also decomposes like calcium carbonate.

$$CuCO_3 \cdot Cu(OH)_2 \xrightarrow{\Delta} 2CuO + CO_2 \uparrow + H_2O \uparrow$$

(f) At about 300°C, ZnCO<sub>3</sub> decomposes to give ZnO and CO<sub>2</sub> gas.

$$ZnCO_3 \xrightarrow{300^{\circ}C} ZnO + CO_2 \uparrow$$

Q. 3. What happens when bicarbonates of calcium and sodium are heated?

Ans. These bicarbonates decompose to give corresponding carbonates.

$$\begin{array}{ccc} \text{Ca(HCO}_3)_2 & \xrightarrow{\Delta} & \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \\ \text{2NaHCO}_3 & \xrightarrow{\Delta} & \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \end{array}$$

- **Q. 4.** What happens when sulphates of the following metals are heated?
  - (a) Sulphates of Na, K, Mg, Ca, Sr, Ba and Pb
  - (b) Sulphates of Ag, Cu, Zn and Fe
  - (c) Ammonium sulphate, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

Ans. (a) Sulphates of these metals lie in hydrated state; when they are heated, dehydration takes place.

$$\begin{array}{c} \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} & \longrightarrow & \text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O} \\ \text{Glauber's salt} \\ \text{MgSO}_4 \cdot 7\text{H}_2\text{O} & \xrightarrow{150^\circ\text{C}} & \text{MgSO}_4 \cdot \text{H}_2\text{O} & \xrightarrow{200^\circ\text{C}} & \text{MgSO}_4 \\ \text{Epsom salt} \\ 2(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) & \xrightarrow{125^\circ\text{C}} & 2\text{CaSO}_4 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O} \\ \text{Gypsum} & & & & & & & & & & & & & \\ \end{array}$$

$$CaO + SO_3 \uparrow \leftarrow \frac{400^{\circ}C}{Anhydrous} 2CaSO_4 + H_2O$$

(b) 
$$Ag_2SO_4 \xrightarrow{923^{\circ}C} 2Ag + SO_2 + O_2$$

$$CuSO_4 \cdot 5H_2O \xrightarrow{100^{\circ}C} CuSO_4 \cdot H_2O \xrightarrow{230^{\circ}C} CuSO_4$$
Blue vitriol White vitriol

$$\begin{array}{c} \text{SO}_3 \uparrow + \text{CuO} \xleftarrow{800^{\circ}\text{C}}|\\ \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{100^{\circ}\text{C}} \text{ZnSO}_4 \cdot \text{H}_2\text{O} \xrightarrow{280^{\circ}\text{C}} \text{ZnSO}_4\\ \text{White vitriol} \\ \text{ZnO} + \text{SO}_3 \uparrow \xleftarrow{800^{\circ}\text{C}}| \end{array}$$

Decomposition of green vitriol is similar to blue and white vitriol.

$$\begin{array}{ccc} \text{FeSO}_4 \cdot 7\text{H}_2\text{O} & \xrightarrow{140^{\circ}\text{C}} & \text{FeSO}_4 \cdot \text{H}_2\text{O} & \xrightarrow{300^{\circ}\text{C}} & \text{FeSO}_4 \\ \text{Green vitriol} & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & \\ & \\ & \\ & & \\ & \\ & & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ &$$

Note: Thermal decomposition of ferric sulphate also gives ferric oxide and SO<sub>3</sub> gas.

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3 \uparrow$$

(c) Ammonium sulphate on heating melts with emission of ammonia gas. On further heating at about 300°C it finally decomposes to NH<sub>3</sub>, N<sub>2</sub> and SO<sub>2</sub> gases.

$$(NH_4)_2SO_4 \longrightarrow NH_4HSO_4 + NH_3\uparrow$$
  
 $3NH_4HSO_4 \longrightarrow NH_3 + N_2 + 3SO_2 + 6H_2O$ 

- Q. 5. Show the effect of heat on the following commercially important compounds:
  - (a) Borax, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O
  - (b) Common alum, K<sub>2</sub>SO<sub>4</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O
  - (c) Red lead, Pb3O4
  - (d) Orthoboric acid, H<sub>3</sub>BO<sub>3</sub>
  - (e) Orthophosphoric acid, H<sub>3</sub>PO<sub>4</sub>
  - (f) Potassium chlorate, KClO<sub>3</sub>
  - (g) Ammonium dichromate, (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
  - (h) Phosphorus acid, H<sub>3</sub>PO<sub>3</sub>
  - (i) Mixture of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub>
  - (i) Ammonium nitrite, NH<sub>4</sub>NO<sub>2</sub>.
- Ans. (a) Borax on heating decomposes to give colourless glassy bead.  $Na_2B_4O_7\cdot 10H_2O\longrightarrow Na_2B_4O_7+10H_2O$

(b) First of all alum melts, undergoes dehydration and finally gives oxides of potassium and aluminium.

$$K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O \longrightarrow K_2SO_4\cdot Al_2(SO_4)_3 + 24H_2O$$

$$K_2O + Al_2O_3 + 4SO_3 \uparrow \leftarrow$$

(c) Red lead on heating at 470°C gives litharge.

$$2Pb_3O_4 \xrightarrow{470^{\circ}C} 6PbO + O_2 \uparrow$$

(d) Orthoboric acid on heating decomposes to give metaboric acid followed by tetraboric acid.

$$\begin{array}{c} \text{H}_{3}\text{BO}_{3} \xrightarrow{100^{\circ}\text{C}} & \text{HBO}_{2} & + & \text{H}_{2}\text{O} \\ \text{Metaboric acid} & + & \text{H}_{2}\text{O} \\ \end{array}$$

$$4\text{HBO}_{2} \xrightarrow{150^{\circ}\text{C}} & \text{H}_{2}\text{B}_{4}\text{O}_{7} & + & \text{H}_{2}\text{O} \\ & \text{Tetraboric acid} & + & \text{Tetraboric acid} \end{array}$$

(e) When orthophosphoric acid is heated at 250°C it changes to pyrophosphoric acid. On heating at 600°C, pyrophosphoric acid decomposes to give metaphosphoric acid.

2H<sub>3</sub>PO<sub>4</sub> 
$$\xrightarrow{250^{\circ}\text{C}}$$
  $\xrightarrow{\text{Pyrophosphoric acid}}$  + H<sub>2</sub>O

Pyrophosphoric acid + H<sub>2</sub>PO<sub>7</sub>  $\xrightarrow{600^{\circ}\text{C}}$  2HPO<sub>3</sub> + H<sub>2</sub>O

Metaphosphoric acid

(f) KClO<sub>3</sub> decomposes to a small extent at 370°C to give oxygen. On further heating the molten mass solidifies which contains both KCl and KClO<sub>4</sub> (potassium perchlorate).

Potassium perchlorate on thermal decomposition yields potassium chloride and oxygen.

$$2KClO_3 \xrightarrow{370^{\circ}C} 2KCl + 3O_2 \uparrow$$

$$4KClO_3 \longrightarrow 3KClO_4 + KCl$$

$$KClO_4 \xrightarrow{650^{\circ}C} KCl + 2O_2 \uparrow$$

(g) Decomposition of ammonium dichromate on heating yields  $N_2$  gas. It is a method of preparation of  $N_2$  gas.

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + 4H_2O + N_2$$

(h) Phosphorus acid on heating gives phosphine and orthophosphoric acid.

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

 Mixture of ammonium sulphate and sodium nitrate on heating gives nitrous oxide, i.e., laughing gas.

$$(NH_4)_2SO_4 + 2NaNO_3 \xrightarrow{\Delta} Na_2SO_4 + 2NH_4NO_3$$
  
 $NH_4NO_3 \longrightarrow N_2O + 2H_2O$ 

(j) Decomposition of ammonium nitrite on heating gives N2 gas.

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

- Q. 6. Show, what happens when the following chlorides are heated?
  - (a) NH<sub>4</sub>Cl
- (b) CuCl<sub>2</sub>·2H<sub>2</sub>O
- (c) MgCl<sub>2</sub>·6H<sub>2</sub>O
- (d) ZnCl<sub>2</sub>·2H<sub>2</sub>O

Ans. (a) Ammonium chloride decomposes to give  $NH_3(g)$  and HCl(g).

$$NH_4Cl(s) \xrightarrow{\Delta} NH_3(g) + HCl(g)$$

(b) Cupric chloride on heating gives cuprous chloride along with Cl<sub>2</sub> gas.

$$\begin{array}{ccc} CuCl_2 \cdot 2H_2O & \longrightarrow CuCl_2 + 2H_2O \\ & 2CuCl_2 & \longrightarrow Cu_2Cl_2 + Cl_2 \end{array}$$

(c) Hydrated zinc chloride when heated gives basic zinc chloride and zinc oxychloride.

$$ZnCl_2 \cdot 2H_2O \longrightarrow Zn(OH)Cl + HCl + H_2O$$
  
 $2ZnCl_2 \cdot H_2O \longrightarrow Zn_2OCl_2 + 2HCl + H_2O$ 

(d) Crystalline magnesium chloride on heating first of all loses its four water molecules. Dihydrate of magnesium chloride when further heated undergoes hydrolysis to give MgO along with HCl.

$$\begin{array}{c} \text{MgCl}_2\text{-}6\text{H}_2\text{O} \longrightarrow \text{MgCl}_2\text{-}2\text{H}_2\text{O} + 4\text{H}_2\text{O} \\ \text{MgCl}_2\text{-}2\text{H}_2\text{O} \xrightarrow{185^\circ\text{C}} \text{Mg(OH)Cl} + \text{HCl} + \text{H}_2\text{O} \\ \text{Mg(OH)Cl} \xrightarrow{600^\circ\text{C}} \text{MgO} + \text{HCl} \end{array}$$

- **Q. 7.** Show, what happens when the following compounds are heated?
  - (a) KMnO<sub>4</sub> (Potassium permanganate)
  - (b) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Potassium dichromate)
  - (c) Plaster of Paris, [(CaSO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O]
  - (d) Na<sub>2</sub>HPO<sub>4</sub> (Disodium hydrogen phosphate)
  - (e) [Na(NH<sub>4</sub>)HPO<sub>4</sub>·4H<sub>2</sub>O] (Microcosmic salt).
- Ans. (a) When KMnO<sub>4</sub> is heated, it decomposes evolving oxygen.

$$2KMnO_4 \xrightarrow{240^{\circ}C} K_2MnO_4 + MnO_2 + O_2$$

(b) Potassium dichromate, on heating strongly, decomposes liberating oxygen.

(c) On heating upto 200°C, it becomes anhydrous. The anhydrous salt decomposes into CaO and SO<sub>3</sub>.

 $4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$ 

$$(CaSO4)2H2O \xrightarrow{200^{\circ}C} 2CaSO4 + H2O$$

$$CaSO4 \xrightarrow{400^{\circ}C} CaO + SO3$$

(d) Disodium hydrogen phosphate on heating first forms sodium pyrophosphate which on further heating forms sodium metaphosphate.

(e) When microcosmic salt is heated, it melts to form a clear transparent mass of sodium metaphosphate. Ammonia gas is evolved.

Na(NH<sub>4</sub>)HPO<sub>4</sub> 
$$\longrightarrow$$
 NaPO<sub>3</sub> + NH<sub>3</sub> + H<sub>2</sub>O
Sodium
metaphosphate

#### IMPORTANT CHEMICAL REACTIONS

- Q. 1. What happens when water reacts with the following compounds?
  - (a) Antimony chloride (SbCl<sub>3</sub>), bismuth chloride (BiCl<sub>3</sub>)
  - (b) Calcium cyanamide, CaCN<sub>2</sub>
  - (c) Calcium phosphide, Ca<sub>3</sub>P<sub>2</sub>
  - (d) Magnesium nitride, Mg<sub>3</sub>N<sub>2</sub>
  - (e) Red hot coke
  - (f) Red hot iron
  - (g) Borax.
- Ans. (a) Chlorides of both antimony and bismuth undergo hydrolysis to give white precipitates of their oxychlorides.

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$
  
 $BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$   
(White ppt.)

- (b) Calcium cyanamide on hydrolysis evolves  $NH_3(g)$ .  $CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3 \uparrow$
- (c) Calcium phosphide undergoes hydrolysis to evolve phosphine gas.

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3\uparrow$$

(d) Magnesium nitride reacts with water to form its hydroxide and ammonia gas.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3\uparrow$$

(e) On passing steam over red hot coke, we get water gas.

$$C + H_2O(g) \longrightarrow \underbrace{CO^{\bullet} + H_2}_{\text{Water gas}}$$

(f) On passing steam over red hot iron, it gives ferrosoferric oxide and H<sub>2</sub> gas.

$$3\text{Fe} + 4\text{H}_2\text{O}(g) \longrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\uparrow$$

(g) Borax undergoes hydrolysis and the solution becomes alkaline due to NaOH.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

- Q. 2. Write down the products when H<sub>2</sub>O<sub>2</sub> reacts with following compounds:
  - (a) PbS (b) KI (c)  $H_2S$  (d)  $O_3$  (e)  $Ag_2O$
  - (f)  $FeSO_4$  (g)  $K_3[Fe(CN)_6]$  (h)  $KMnO_4$  (i)  $Cl_2$ .
- Ans. (a) Lead sulphide is oxidised to lead sulphate by H<sub>2</sub>O<sub>2</sub>.

$$\begin{array}{c}
4 \times [\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + [\text{O}]] \\
\text{PbS} + 4[\text{O}] \longrightarrow \text{PbSO}_4
\end{array}$$

$$\begin{array}{c}
\text{PbS} + 4\text{H}_2\text{O}_2 \longrightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}}$$

- (b) On adding KI to H<sub>2</sub>O<sub>2</sub>, I<sub>2</sub> is liberated.
  - $2KI + H_2O_2 \longrightarrow 2KOH + I_2$

(c) Hydrogen peroxide oxidises H2S to sulphur.

$$\begin{array}{c} H_2O_2 \longrightarrow H_2O + [O] \\ H_2S + [O] \longrightarrow H_2O + S \\ \end{array}$$

$$H_2O_2 + H_2S \longrightarrow 2H_2O + S$$

(d) Mutual reduction of H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> takes place according to the following reaction.

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

(e) Hydrogen peroxide reduces Ag<sub>2</sub>O to silver metal.

$$H_2O_2 \longrightarrow H_2O + [O]$$

$$Ag_2O \longrightarrow 2Ag + [O]$$

$$[O] + [O] \longrightarrow O_2$$

$$H_2O_2 + Ag_2O \longrightarrow 2Ag + H_2O + O_2$$

(f) Ferrous sulphate is oxidised to ferric sulphate by H2O2.

$$\frac{H_2O_2 \longrightarrow H_2O + [O]}{2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O}$$
$$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$$

(g) In alkaline medium,  $K_3[Fe(CN)_6]$  is reduced to  $K_4[Fe(CN)_6]$  by  $H_2O_2$ .

$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 \longrightarrow 2K_4[Fe(CN)_6] + O_2 + 2H_2O$$

(h) H<sub>2</sub>O<sub>2</sub> decolourises the pink colour of KMnO<sub>4</sub> solution.

$$5 \times [H_2O_2 \longrightarrow H_2O + [O]]$$

$$2KMnO4 + 3H2SO4 \longrightarrow K2SO4 + 2MnSO4 + 3H2O + 5[O]$$

$$5 [O] + 5[O] \longrightarrow 5O2$$

 $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O_4$ 

 When Cl<sub>2</sub> is passed through H<sub>2</sub>O<sub>2</sub>, mutual reduction takes place.

$$H_2O_2 + Cl_2 \longrightarrow 2HCl + O_2$$

- Q. 3. What happens when CO<sub>2</sub> reacts with the following compounds?
  - (a) Na<sub>2</sub>CO<sub>3</sub>
- (b) Lime water, Ca(OH)<sub>2</sub>

(c) Mg

(d) Na.

**Ans.** (a) By passing CO<sub>2</sub> through aqueous Na<sub>2</sub>CO<sub>3</sub>, it is converted to bicarbonate.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

- (b)  $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$
- (c) Mg burns in the gas jar of CO<sub>2</sub>, forming its oxide and particles of carbon.

$$2Mg + CO_2 \longrightarrow 2MgO + C$$

(d) On heating Na in a gas jar of CO<sub>2</sub>, formation of sodium carbonate takes place.

$$4Na + 3CO_2 \longrightarrow 2Na_2CO_3 + C$$

- Q. 4. What happens when N<sub>2</sub> reacts with the following compounds?
  - (a) Mg (b) CaC<sub>2</sub> (c) Coke and alumina.
- Ans. (a) On passing  $N_2$  over hot Mg we get nitride.

$$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$$

(b) By passing N<sub>2</sub> over red hot CaC<sub>2</sub> we get calcium cyanamide which is used as nitrolim fertilizer.

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

(c) When N<sub>2</sub> is passed through red hot coke and aluminium we get nitride of aluminium.

$$Al_2O_3 + N_2 + C \longrightarrow 2AlN + 3CO$$

- Q. 5. What happens when NO gas is passed through?
  - (a) FeSO<sub>4</sub>

- (b) Na<sub>2</sub>CO<sub>3</sub>.
- Ans. (a) FeSO<sub>4</sub> forms reddish-brown compound with NO called nitrosoferrous sulphate.

$$FeSO_4 + NO \longrightarrow FeSO_4 \cdot NO$$

(b) On passing a mixture of NO and NO<sub>2</sub> through aqueous washing soda we get sodium nitrite.

$$Na_2CO_3 + NO + NO_2 \longrightarrow 2NaNO_2 + CO_2$$

**Q. 6.** Show how carbon monoxide (CO) reacts with Cl<sub>2</sub> and cupric oxide?

Ans. CO gas combines with chlorine to give phosgene.

$$CO + Cl_2 \longrightarrow COCl_2$$

Carbon monoxide reduces cupric oxide to copper.

$$CuO + CO \longrightarrow Cu + CO_2$$

- Q. 7. What happens when caustic soda or caustic potash reacts with?
  - (a) Zn (b) Pb (c) Sn (d) Al (e) Yellow P (f) Sulphur
  - (g) Chlorine, bromine or iodine (h) ZnSO<sub>4</sub>, ZnCl<sub>2</sub> (i) Al<sub>2</sub>O<sub>3</sub>
  - (j) CuSO<sub>4</sub> (k) AgNO<sub>3</sub> (l) SnCl<sub>2</sub> (m) NaNO<sub>3</sub> and Al (n) HgCl<sub>2</sub>
  - (o) Ammonium salts.
- Ans. (a) H<sub>2</sub> gas is evolved when Zn reacts with caustic soda.

 $2NaOH + Zn \longrightarrow Na_2ZnO_2 + H_2\uparrow$ 

(b) Pb reacts with NaOH, just like Zn.

$$2NaOH + Pb \longrightarrow Na_2PbO_2 + H_2$$

(c) Tin dissolves in NaOH to form sodium stannate along with H<sub>2</sub> gas.

$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2\uparrow$$

(d) On boiling aluminium powder with NaOH we get sodium metaaluminate and aluminate.

- (e) Yellow phosphorus reacts with alkali to give phosphine.  $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$
- (f) Sulphur dissolves in alkali to give sodium pentasulphide and sodium thiosulphate.

$$12S + 6NaOH \longrightarrow Na_2S_2O_3 + 2Na_2S_5 + 3H_2O$$

(g) Chlorine, bromine or iodine reacts with alkali in similar

$$\begin{array}{c} Cl_2 + 2NaOH(dil.) \longrightarrow \ NaCl + NaClO + H_2O \\ 3Cl_2 + 6NaOH(conc.) \longrightarrow 5NaCl + NaClO_3 + 3H_2O \\ Similarly, \end{array}$$

$$Br_2 + 2NaOH(dil.) \longrightarrow NaBr + NaBrO + H_2O$$
  
 $3Br_2 + 6NaOH(conc.) \longrightarrow 5NaBr + NaBrO_3 + 3H_2O$   
 $I_2 + 2NaOH(dil.) \longrightarrow NaI + NaIO + H_2O$   
 $3I_2 + 6NaOH(conc.) \longrightarrow 5NaI + NaIO_3 + 3H_2O$ 

(h) When salts of Zn are treated with NaOH, white precipitate of hydroxide is formed which dissolves in excess of NaOH.

(i) Al<sub>2</sub>O<sub>3</sub> dissolves in NaOH forming sodium metaaluminate.

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

(j) CuSO<sub>4</sub> forms precipitate of Cu(OH)<sub>2</sub>, when added to NaOH.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + 2Na_2SO_4$$

- (k) AgNO<sub>3</sub> on treatment with NaOH, gives precipitate of Ag<sub>2</sub>O.  $2AgNO_3 + 2NaOH \longrightarrow 2NaNO_3 + Ag_2O + H_2O$ (ppt.)
- (1) SnCl<sub>2</sub> dissolves in NaOH to give white precipitate of Sn(OH)<sub>2</sub>. Precipitate dissolves in excess of NaOH.

$$SnCl_2 + 2NaOH \longrightarrow 2NaCl + Sn(OH)_2$$
(White ppt.)

$$Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$$

- (m)  $3NaNO_3 + 8AI + 5NaOH + 2H_2O \longrightarrow 8NaAlO_2 + 3NH_3$
- (n) On heating with NaOH solution, mercuric chloride forms a yellow precipitate of mercuric oxide.

$$HgCl_2 + 2NaOH \longrightarrow HgO + 2NaCl + H_2O$$

(o) Ammonium salts on heating with NaOH solution, liberate NH<sub>3</sub> gas.

$$NH_4Cl + NaOH \longrightarrow NH_3 + NaCl + H_2O$$
Ammonium
chloride

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 + 2H_2O$$

- **O. 8.** What happens when?
  - (a) SO<sub>2</sub> gas is passed through a suspension of iodine in water.
  - (b) Metallic zinc is added to alkaline sodium nitrite solution.
- (a) SO<sub>2</sub> reduces I<sub>2</sub> to HI and itself undergoes oxidation to H<sub>2</sub>SO<sub>4</sub>.  $SO_2 + I_2 + 2H_2O \longrightarrow H_2SO_4 + 2HI$

(b) 
$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + 2[H]$$
  
 $NaNO_2 + 6[H] \xrightarrow{Zn/NaOH} NaOH + NH_3 + H_2O$ 

Q. 9. What happens when ozone reacts with?

- (a) Hg (b) Ag (c)  $K_4[Fe(CN)_6]$ (d)  $K_2MnO_4$
- (e) KI (f) PbS (g) S (h) P.

(a) Mercury is oxidised to mercurous oxide, which sticks to the Ans. walls of the glass vessel.

$$\begin{array}{c} O_3 \longrightarrow O_2 + [O] \\ 2Hg + [O] \longrightarrow Hg_2O \\ \hline 2Hg + O_3 \longrightarrow O_2 + Hg_2O \end{array}$$

(b) Silver is oxidised to its oxide.

$$\begin{array}{c} O_3 \longrightarrow O_2 + [O] \\ 2Ag + [O] \longrightarrow Ag_2O \\ 2Ag + O_3 \longrightarrow Ag_2O + O_2 \end{array}$$

(c) Potassium ferrocyanide is oxidised to potassium ferricyanide.

$$\begin{array}{c} O_3 \longrightarrow O_2 + [O] \\ 2K_4[Fe(CN)_6] + H_2O + [O] \longrightarrow 2K_3[Fe(CN)_6] + 2KOH \end{array}$$

$$2K_3[re(CN)_6] + R_2O + [O] \longrightarrow 2K_3[re(CN)_6] + 2KON$$

$$2K_4[Fe(CN)_6] + O_3 + H_2O \longrightarrow 2K_3[Fe(CN)_6] + 2KOH + O_2$$
  
(d) Potassium manganate is converted to potassium permanganate

by passing O<sub>3</sub> gas through its aqueous solution.

2KI + 
$$H_2O$$
 +  $O_3$   $\longrightarrow$  2KOH +  $I_2$  +  $O_2$ 

(f) Lead sulphide is oxidised to lead sulphate.

$$4 \times [O_3 \longrightarrow O_2 + [O]]$$

$$PbS + 4[O] \longrightarrow PbSO_4$$

$$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$$

(g) Sulphur is oxidised to sulphuric acid in aqueous medium.

$$3 \times [O_3 \longrightarrow O_2 + [O]]$$

$$S + 3[O] \longrightarrow SO_3$$

$$H_2O + SO_3 \longrightarrow H_2SO_4$$

$$3O_3 + S + H_2O \longrightarrow H_2SO_4 + 3O_2$$

(h) Ozone oxidises phosphorus to phosphorus pentoxide which dissolves in water to give orthophosphoric acid.

$$5 \times [O_3 \longrightarrow O_2 + [O]] 
2P + 5[O] \longrightarrow P_2O_5 
P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

$$2P + 5O_3 + 3H_2O \longrightarrow 2H_3PO_4 + 5O_2$$

- **Q.10.** What happens when?
  - (a) Mixture of red phosphorus and iodine is heated with
  - (b) Calcium phosphate is heated with sand and coke.
  - (c) Phosphorus is heated with sulphur.
  - (d) Aqua-regia is added to gold.

(a) On boiling the mixture of red P and I2 with water, we get Ans. hydrogen iodide and phosphorus acid.

$$\begin{array}{c}
2P + 3I_2 \longrightarrow 2PI_3 \\
[PI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HI] \times 2\\
\hline
2P + 3I_2 + 6H_2O \longrightarrow 2H_3PO_3 + 6HI
\end{array}$$

(b) It is a method of preparation of white phosphorus.

$$Ca_3(PO_4)_2 + 3SiO_2 \longrightarrow 3CaSiO_3 + P_2O_5$$
  
 $P_2O_5 + 5C \longrightarrow 2P + 5CO\uparrow$ 

(c) When phosphorus reacts with sulphur we get tri- and pentasulphides, which are used in the tip of matchstick.

$$4P + 6S \longrightarrow 2P_2S_3$$

$$4P + 10S \longrightarrow 2P_2S_5$$

Ans.

(d) Gold dissolves in aqua-regia to form chloroauric acid.

$$\begin{array}{l} 3\times [HNO_3+3HCl \longrightarrow NOCl+2H_2O+2[Cl]] \\ 2\times [Au+3[Cl] \longrightarrow AuCl_3] \\ 2\times [AuCl_3+HCl \longrightarrow H[AuCl_4]] \end{array}$$

 $3HNO_3 + 2Au + 11HCl \longrightarrow 3NOCl + 6H_2O + 2H[AuCl_4]$ 

Q.11. What happens when ammonia reacts with?

- (a) Silver nitrate
- (b) Silver chloride
- (c) Copper sulphate
- (d) Iodine
- (e) Zinc chloride
- (f) Nessler's reagent
- (g) Mercurous chloride
- (h) Sodium

(i) CuO

- (j) Chlorine
- (k) Bromine.
- (a) Silver nitrate dissolves in ammonia solution forming complex.
   AgNO<sub>3</sub> + 2NH<sub>4</sub>OH → [Ag(NH<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> + 2H<sub>2</sub>O

Diamminesilver nitrate
(b) Silver chloride also dissolves in ammonia forming complex

compound. 
$$\begin{array}{c} AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl \\ Diamminesilver(I) \\ chloride \end{array} + 2H_2O$$

(c) When ammonia solution is added to copper sulphate, we get dark blue coloured complex compound.

$$CuSO_4 + 4NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$$
Tetraamminecopper(II)
sulphate

(d) Iodine forms an explosive compound with ammonia.
 2NH<sub>3</sub> + 3I<sub>2</sub> → NH<sub>3</sub>NI<sub>3</sub> + 3HI

(e) When ammonia solution is added to zinc chloride we get white precipitate which dissolves in excess of ammonia solution.

$$ZnCl_2 + 2NH_4OH \longrightarrow Zn(OH)_2 + 2NH_4Cl$$

$$Zn(OH)_2 + 2NH_4OH + 2NH_4Cl \longrightarrow [Zn(NH_3)_4]Cl_2 + 4H_2O$$

$$ZnCl_2 + 4NH_4OH \longrightarrow [Zn(NH_3)_4]Cl_2 + 4H_2O$$
Tetraamminezinc

(f) Nessler's reagent is used to test ammonia. It gives brown precipitate of iodide of Millon's base when ammonia gas is passed through it.

$$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow Hg O + 7KI + 2H_2O$$

Iodide of Millon's base

(g) White precipitate of mercurous chloride dissolves in ammonia solution and gives black residue of basic mercuric chloride and mercury.

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underbrace{HgNH_2Cl + Hg}_{Black ppt.} + NH_4Cl + 2H_2O$$

(h) Sodium dissolves in liquid ammonia forming blue coloured solution due to presence of solvated electrons.

Na + 
$$(x + y)NH_3 \longrightarrow Na(NH_3)_x^+ + (NH_3)_y^+$$
  
(Solvated electrons)

When dry  $NH_3(g)$  comes in contact with sodium, it gives nascent hydrogen which is used to reduce various organic compounds.

$$Na + NH_3(g) \longrightarrow NaNH_2 + [H]$$

(i) Red hot cupric oxide reduces NH3 gas to nitrogen.

$$3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O$$

(j) Chlorine oxidises ammonia (excess) to nitrogen.

$$8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

When chlorine is in excess, ammonia reacts with it to form an explosive.

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

(k) Reaction of Br<sub>2</sub> with ammonia is similar to the reaction of Cl<sub>2</sub> with ammonia.

$$\begin{array}{l} 8NH_3 + 3Br_2 {\longrightarrow} \ N_2 + 6NH_4Br \\ NH_3 + 3Br_2 {\longrightarrow} \ NBr_3 + 3HBr \end{array}$$

Q.12. What happens when?

- (a) Sodium thiosulphate is added to silver nitrate.
- (b) Nitrogen is passed through red hot alumina and coke.
- (c) Iodine is added to the mixture of Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S.
- (d) Ammonium thiocyanate is added to ferric chloride.

Ans. (a) Formation of complex compound takes place.

$$2Na_2S_2O_3 + AgNO_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaNO_3$$

b)  $Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO\uparrow$ 

(c) Iodine reacts with the mixture of Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S to form sodium thiosulphate.

$$Na_2S + Na_2SO_3 + I_2 \longrightarrow Na_2S_2O_3 + 2NaI$$

(d) Ammonium thiocyanate is the reagent to test ferric ion; formation of blood red coloured ferric thiocyanate takes place.

$$FeCl_3 + 3NH_4SCN \longrightarrow Fe(SCN)_3 + 3NH_4Cl$$
Blood red

- **Q.13.** Write down the reaction product of chlorine with the following compounds. Give the involved reactions also.
  - (a) Mixture of alumina and coke
  - (b) Phosphine
  - (c) Iodine in aqueous medium
  - (d) Carbon monoxide
  - (e) Lime
  - (f) H<sub>2</sub>S gas
  - (g) KI
  - (h) Hypo (sodium thiosulphate).

Ans. (a)  $Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO\uparrow$ 

(b) Phosphine burns in atmosphere of chlorine, forming PCl<sub>5</sub> and HCl.

$$PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$$

(c) Chlorine oxidises iodine to iodic acid in aqueous medium.

$$\begin{split} & [\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HCl} + [\text{O}]] \times 5 \\ & \text{I}_2 + 5[\text{O}] \longrightarrow \text{I}_2\text{O}_5 \\ & \text{I}_2\text{O}_5 + \text{H}_2\text{O} \longrightarrow 2\text{HIO}_3 \\ \hline & \text{I}_2 + 5\text{Cl}_2 + 6\text{H}_2\text{O} \longrightarrow 2\text{HIO}_3 + 10\text{HCl} \end{split}$$

(d) Chlorine combines with carbon monoxide to form a poisonous gas phosgene.

$$CO(g) + Cl_2(g) \longrightarrow COCl_2$$
Phosgene

(e) **Lime:** (i) On passing Cl<sub>2</sub> gas through hot and concentrated lime water we get calcium chloride and calcium chlorate.

$$6\text{Ca}(\text{OH})_2 + 6\text{Cl}_2 \longrightarrow 5\text{Ca}\text{Cl}_2 + \text{Ca}(\text{ClO}_3)_2 + 6\text{H}_2\text{O}$$
Calcium chlorate

(ii) Cl<sub>2</sub> gas gives calcium hypochloride on passing through cold and dilute lime water.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + Ca(OCl)_2 + 2H_2O$$

(iii) On passing Cl<sub>2</sub> through dry lime we get bleaching powder.

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$
(Bleaching powder)

(f) On passing mixture of Cl<sub>2</sub> and H<sub>2</sub>S through a hot tube, oxidation of H<sub>2</sub>S to sulphur takes place.

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

(g) Chlorine is more reactive than iodine, hence, it displaces iodine from iodide salts.

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

(h) Chlorine water oxidises sodium thiosulphate to sodium sulphate.

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

$$Na_2S_2O_3 + [O] \longrightarrow Na_2SO_4 + S$$

$$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl + S$$

#### Q.14. What happens when?

- (a) Iodine is added to sodium thiosulphate.
- (b) Iodine is dissolved in aqueous solution of KI.
- (c) Iodine is added to stannous chloride in acid medium.
- (d) Iodine is allowed to react with aq. KOH.

(a) Iodine changes sodium thiosulphate to sodium tetrathionate.  $2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$ 

(b) Iodine dissolves in aqueous KI forming potassium triiodide.  $KI + I_2 \rightarrow KI_3$ 

(c) Iodine oxidises SnCl2 to SnCl4.

$$SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI$$

(d) Iodine converts cold and dilute KOH to potassium hypoiodite.

$$2KOH + I_2 \longrightarrow KI + KIO + H_2O$$

With hot KOH, Iodine forms KI and potassium iodate.

$$6\text{KOH} + 3\text{I}_2 \longrightarrow 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O}$$

#### Q.15. What happens when:

- (a) Chromium hydroxide is treated with hydrogen peroxide in the presence of sodium hydroxide.
- (b) Hydrolith is treated with water.
- (c) Concentrated solution of NH<sub>4</sub>HSO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> is electrolysed using current of high density.
- (d) Hydrazine reacts with hydrogen peroxide.
- (e) Tin tetrachloride reacts with lithium aluminium hydride.
- (f) Sodium hydride reacts with diborane.
- (g) Anhydrous potassium nitrate is heated with excess of metallic potassium.
- (h) Beryllium chloride reacts with LiAlH<sub>4</sub>.
- (i) A mixture of borax and cobalt oxide is heated in a flame.
- (j) Tin is treated with concentrated nitric acid.
- (k) Red lead is treated with nitric acid.
- (l) Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with
- (m) Lead is reacted with acetic acid in presence of oxygen.
- (n) Stannous chloride is reacted with mercuric chloride
- (o) Potassium ferrocyanide is heated with concentrated
- (p) Silica is heated with CaF<sub>2</sub> and concentrated H<sub>2</sub>SO<sub>4</sub>.
- (q) Phosphine is treated with an acidified copper sulphate
- (r) Iodine reacts with concentrated nitric acid.
- (s) Orthophosphoric acid is heated with conc. nitric acid and ammonium molybdate.
- (t) Disodium hydrogen phosphate is added to ammonical solution of magnesium sulphate.
- (u) Phosphine is passed through silver nitrate solution.
- (v) Ammonia reacts with sodium hypochlorite.

- (w) Copper sulphate is treated with hypophosphorus acid.
- (x) Mercuric chloride is treated with hypophosphorus acid.
- (y) Phosphorus pentachloride reacts with sulphuric acid.
- (z) Phosphoric acid reacts with Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F.

(a) Chromium hydroxide is converted into soluble sodium Ans. chromate.

$$2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$

(b) Hydrolysis of CaH2 occurs with evolution of hydrogen.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2\uparrow$$

(c) Ammonium peroxydisulphate is formed.

$$NH_4HSO_4 \iff H^+ + NH_4SO_4^-$$

 $2\mathrm{NH_4SO_4^-} \longrightarrow (\mathrm{NH_4})_2\mathrm{S}_2\mathrm{O}_8 \ + \ 2e$ At anode:  $2H^+ + 2e \longrightarrow H_2$ 

At cathode:

(d) Hydrazine is oxidised to N2 and H2O.

$$N_2H_4 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$$

(e) Tin hydride is formed.

$$SnCl_4 + LiAlH_4 \longrightarrow SnH_4 + LiCl + AlCl_3$$

(f) Sodium hydride reacts with diborane to form sodium borohydride.

$$2NaH + B_2H_6 \longrightarrow 2NaBH_4$$

(g) Nitrogen is released with the formation of K2O.

$$2KNO_3 + 10K \longrightarrow N_2 + 6K_2O$$

(h) Beryllium hydride is formed.

$$2\text{BeCl}_2 + \text{LiAlH}_4 \longrightarrow 2\text{BeH}_2 + \text{LiCl} + \text{AlCl}_3$$

 $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{-10H_2O} Na_2B_4O_7 \longrightarrow$ 

$$2NaBO_2 + B_2O_3$$

Boron anhydride combines with cobalt oxide to form cobalt metaborate.

Sn dissolves in conc. HNO<sub>3</sub> forming metastannic acid.

Sn + 4HNO<sub>3</sub> 
$$\longrightarrow$$
 H<sub>2</sub>SnO<sub>3</sub> + 4NO<sub>2</sub> + H<sub>2</sub>O  
Metastannic  
acid

(k) Red lead, when treated with conc. HNO3, forms lead nitrate and brownish black insoluble PbO2. This indicates that red lead is a mixed oxide containing PbO and PbO<sub>2</sub>.

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

(1) CO<sub>2</sub> reacts with ammonium hydroxide to form ammonium bicarbonate, which then reacts with NaCl to form sodium bicarbonate. This is Solvay's process for manufacture of washing soda.

$$NH_4OH + CO_2 \longrightarrow NH_4HCO_3$$
  
 $NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$ 

(m) Lead dissolves in acetic acid in presence of oxygen in the form of lead acetate.

Pb + 2CH<sub>3</sub>COOH + 
$$\frac{1}{2}$$
O<sub>2</sub>  $\longrightarrow$  Pb(CH<sub>3</sub>COO)<sub>2</sub> + H<sub>2</sub>O

(n) Redox reaction occurs SnCl<sub>2</sub> first reduces HgCl<sub>2</sub> to Hg<sub>2</sub>Cl<sub>2</sub> and then into Hg.

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4;$$
  
 $Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$ 

(o) Carbon monoxide is evolved when potassium ferrocyanide is heated with conc. H2SO4.

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

(p) H<sub>2</sub>SO<sub>4</sub> evolves H<sub>2</sub>F<sub>2</sub> from CaF<sub>2</sub> which reacts with silica to form silicon tetrafluoride.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2F_2;$$
  
 $SiO_2 + 2H_2F_2 \longrightarrow SiF_4 + 2H_2O$ 

(q) Copper phosphide is formed.

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

(r) Iodine is oxidised to iodine pentoxide which combines with water to form iodic acid.

 $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$ 

(s) This is a test of phosphate ion. A yellow canary precipitate of ammonium phosphomolybdate is formed.

 $H_3PO_4 + 21HNO_3 + 12(NH_4)_3MoO_4 \longrightarrow$ 

 $(NH_4)_3PO_4\cdot 12MoO_3 + 21NH_4\cdot NO_3 + 12H_2O_3$ 

(t) This is a test of magnesium ion. A white precipitate magnesium ammonium phosphate is formed.

$$MgSO_4 + Na_2HPO_4 + NH_4OH \longrightarrow MgNH_4PO_4$$

+ Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O

(u) Silver phosphide is formed.

$$3AgNO_3 + PH_3 \longrightarrow Ag_3P + 3HNO_3$$

(v) Ammonia is oxidised to nitrogen.

$$2NH_3 + 3NaClO \longrightarrow N_2 + 3NaCl + 3H_2O$$

or when a strong aqueous solution of ammonia is boiled with sodium hypochlorite in presence of glue, hydrazine is formed.

$$2NH_3 + NaClO \longrightarrow NH_2 \longrightarrow NH_2 + NaCl + H_2O$$

(w) Copper sulphate is reduced to cuprous hydride.

$$4\text{CuSO}_4 + 3\text{H}_3\text{PO}_2 + 6\text{H}_2\text{O} \longrightarrow 2\text{Cu}_2\text{H}_2 + 3\text{H}_3\text{PO}_4$$

+ 4H<sub>2</sub>SO

Ans.

 (x) Mercuric chloride is réduced to mercurous chloride and finally to metallic mercury.

$$2HgCl_2 + H_3PO_2 + 2H_2O \longrightarrow 2Hg + H_3PO_4 + 4HCl$$

(y) Hydroxyl groups of H<sub>2</sub>SO<sub>4</sub> are replaced by chlorine atoms to form sulphuryl chloride.

$$SO_2(OH)_2 + PCl_5 \longrightarrow SO_2Cl_2 + POCl_3 + 2HCl$$
  
Sulphuric acid Sulphuryl chloride

(z) Hydrofluoric acid is evolved.

 $Ca_5(PO_4)_3F + 7H_3PO_4 + 5H_2O \longrightarrow 5Ca(H_2PO_4)_2 \cdot H_2O + HF$  **Q.16.** What happens when:

- (i) Sulphur dioxide is bubbled through aqueous solution of copper sulphate in presence of potassium thiocyanate.
- (ii) Hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide.
- (iii) Hydrogen sulphide is passed through acidified ferric chloride solution.
- (iv) Hydrogen sulphide is passed through sodium bisulphite solution.
- (v) Potassium chlorate is heated with conc. H<sub>2</sub>SO<sub>4</sub>.
- (vi) Arsine is passed through silver nitrate solution.
- (vii) Sodium chloride and manganese dioxide mixture is heated with conc. H<sub>2</sub>SO<sub>4</sub>.
- (viii) Silver bromide is treated with hypo solution.
- (ix) Cupric chloride is heated with copper turnings and conc. HCl.
- (x) Silver chloride is treated with aqueous NaCN and the product is treated with zinc in alkaline solution.
- (xi) Potassium ferrocyanide solution is added to a solution of ferric chloride.
- (xii) Metal chloride is heated with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and conc. H<sub>2</sub>SO<sub>4</sub>.
- (xiii) Sodium iodate is reacted with sodium bisulphite.
- (xiv) Copper sulphate is treated with potassium iodide followed by addition of hypo solution.
- (xv) A mixture of silver chloride and sodium carbonate is heated.

- (xvi) Potassium iodide is added to bleaching powder containing dilute acetic acid.
- (xvii) Xenon hexafluoride is hydrolysed.
- (xviii) Potassium nitrite reacts with cobalt chloride in presence of acetic acid.
- (xix) Potassium iodide is added in excess to the solution of ferric sulphate.
- (xx) Copper is left in moist air.
- (xxi) Water reacts with Al<sub>4</sub>C<sub>3</sub>.
- (xxii) Water reacts with XeF<sub>4</sub>.
- (xxiii) Water reacts with NCl<sub>3</sub>.

(i) A white precipitate of cuprous thiocyanate is formed.  $2\text{CuSO}_4 + \text{SO}_2 + 2\text{KCNS} + 2\text{H}_2\text{O} \longrightarrow 2\text{CuCNS} + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$ 

(ii) Sulphur is precipitated.

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

(iii) Reduction of FeCl<sub>3</sub> occurs with precipitation of sulphur.  $H_2S + 2FeCl_3 \longrightarrow 2FeCl_2 + 2HCl + S$ 

(iv) Sulphur is precipitated.

$$2NaHSO_3 \longrightarrow Na_2SO_3 + H_2O + SO_2$$
  
 $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$ 

(v) Chlorine dioxide is evolved with explosion.

$$3KClO_3 + 3H_2SO_4 \longrightarrow 3KHSO_4 + HClO_4$$

+ 2ClO<sub>2</sub> + H<sub>2</sub>O

(vi) Black precipitate of silver is obtained. AsH<sub>3</sub> acts as a reducing agent.

$$AsH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3AsO_3$$

(vii) Chlorine gas is evolved.

$$\begin{aligned} [\text{NaCl} + \text{H}_2\text{SO}_4 &\longrightarrow \text{NaHSO}_4 + \text{HCl}] \times 2 \\ \text{MnO}_2 + \text{H}_2\text{SO}_4 &\longrightarrow \text{MnSO}_4 + \text{H}_2\text{O} + [\text{O}] \\ 2\text{HCl} + [\text{O}] &\longrightarrow \text{Cl}_2 + \text{H}_2\text{O} \end{aligned}$$

$$2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4$$

+ 2H<sub>2</sub>O + Cl<sub>2</sub>

(viii) Silver bromide dissolves in hypo solution forming sodium argentothiosulphate.

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

- (ix) White precipitate of  $Cu_2Cl_2$  (cuprous chloride) is formed.  $CuCl_2 + Cu \longrightarrow Cu_2Cl_2$
- (x) AgCl dissolves in NaCN forming sodium argenocyanide complex. Zinc displaces silver from this complex being more electropositive in nature.

$$AgCl + 2NaCN \longrightarrow Na[Ag(CN)_2] + NaCl 2Na[Ag(CN)_2] + Zn \longrightarrow Na_2Zn(CN)_4 + 2Ag$$

(xi) Dark blue coloured precipitate (prussian blue) of ferri-ferrocyanide is obtained.

$$4\text{FeCl}_3 + 3\text{K}_4\text{Fe}(\text{CN})_6 \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl}$$
  
Ferri-ferrocyanide

(xii) Reddish yellow vapours of chromyl chloride are evolved.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

$$[KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl] \times 4$$

$$2CrO_3 + 4HCl \longrightarrow 2CrO_2Cl_2 + 2H_2O$$

$$\begin{array}{l} \text{K}_2\text{Cr}_2\text{O}_7 + 6\text{H}_2\text{SO}_4 + 4\text{KCl} \longrightarrow 2\text{CrO}_2\text{Cl}_2 \\ + 6\text{KHSO}_4 + 3\text{H}_2\text{O} \end{array}$$

(xiii) Iodine is formed.

$$2NaIO_3 + 5NaHSO_3 \longrightarrow 3NaHSO_4 + 2Na_2SO_4$$

 $+ H_2O + I_2$ 

(xiv) Iodine is first evolved which reacts with hypo forming sodium tetrathionate and sodium iodide. White precipitate of cuprous iodide is formed.

$$\begin{array}{c} \text{CuSO}_4 + 2\text{KI} \longrightarrow \text{CuI}_2 + \text{K}_2\text{SO}_4 \\ 2\text{CuI}_2 \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2 \\ \text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \end{array}$$

(xv) A mixture of silver chloride and sodium carbonate when heated forms silver carbonate which decomposes to give

$$2 \text{AgCl} + \text{Na}_2 \text{CO}_3 \xrightarrow{\Delta} \text{Ag}_2 \text{CO}_3 + 2 \text{NaCl}$$

$$\text{Ag}_2 \text{CO}_3 \xrightarrow{\Delta} 2 \text{Ag} + \text{CO}_2 + \frac{1}{2} \text{O}_2$$

(xvi) Iodine is liberated.

$$\begin{array}{c} \text{CaOCl}_2 + 2\text{CH}_3\text{COOH} \longrightarrow (\text{CH}_3\text{COO})_2\text{Ca} + \text{H}_2\text{O} + \text{Cl}_2 \\ 2\text{KI} + \text{Cl}_2 \longrightarrow 2\text{KCl} + \text{I}_2 \end{array}$$

(xvii) Xenon trioxide (an explosive) is formed.

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

(xviii) Yellow precipitate of potassium cobaltinitrite is formed. The following reactions occur.

$$\begin{array}{c} \text{CoCl}_2 + 2\text{KNO}_2 \longrightarrow \text{Co(NO}_2)_2 + 2\text{KCl} \\ \text{Co(NO}_2)_2 + 4\text{KNO}_2 \longrightarrow \text{K}_4\text{Co(NO}_2)_6 \\ \text{Pot. cobaltinitrite} \\ \text{KNO}_2 + \text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COOK} + \text{HNO}_2 \\ 2\text{HNO}_2 \longrightarrow 2\text{NO} + \text{H}_2\text{O} + [\text{O}] \\ 2\text{K}_4\text{Co(NO}_2)_6 + \text{H}_2\text{O} + [\text{O}] \longrightarrow 2\text{K}_3\text{Co(NO}_2)_6 + 2\text{KOH} \\ \text{Pot. cobaltinitrite} \end{array}$$

(xix) Ferric sulphate is reduced to ferrous sulphate with liberation of iodine.

$$Fe_2(SO_4)_3 + 2KI \longrightarrow 2FeSO_4 + K_2SO_4 + I_2$$

(xx) Copper in presence of moisture, oxygen and CO<sub>2</sub> of the atmosphere is reacted on the surface and a green layer of basic carbonate is deposited on its surface.

This is the method of preparation of methane.

(xxii) Xenon trioxide (an explosive substance) is formed.

$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + \frac{3}{2}O_2 + 12HF$$

(xxiii) Ammonia and hypochlorous acid are formed.

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$$

#### CONVERSION OF COMPOUNDS

- Q. 1. How will you bring about the following conversions?
  - (i) Sodium bicarbonate from sodium chloride.
  - (ii) Hypo from sodium sulphate.
  - (iii) Caustic soda from sodium carbonate.
  - (iv) Sodium bicarbonate from sodium carbonate.
  - (v) Sodium thiosulphate from sodium sulphite.
  - (vi) Hydrobromic acid from potassium bromide.
  - (vii) Chlorine from potassium chlorate.
  - (viii) Ammonia from nitre.
  - (ix) Nitric oxide from nitre.
  - (x) Oxygen from nitre.
- (i) This conversion is made in Solvay's process. Brine is first Ans. of all saturated by ammonia. By passing CO2 gas through ammonia-saturated brine, we get sodium bicarbonate.

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$
  
 $NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$ 

Note: On heating sodium bicarbonate, sodium carbonate is obtained.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2 \uparrow$$

(ii) On heating sodium sulphate with coke, we get sodium sulphide.

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO\uparrow$$

When SO<sub>2</sub> gas is passed through the mixture of Na<sub>2</sub>S and Na<sub>2</sub>CO<sub>3</sub>, we get hypo.

$$2Na_2S + Na_2CO_3 + 4SO_2 \longrightarrow 3Na_2S_2O_3 + CO_2 \uparrow$$
  
Sodium thiosulphate

(iii) By mixing Na<sub>2</sub>CO<sub>3</sub> with lime water, we get caustic soda along with white residue of CaCO<sub>3</sub>.

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$
(Caustic soda)

(iv) By passing CO2 gas through Na2CO3 in aqueous medium, we get sodium bicarbonate.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

(v) On boiling sodium sulphite with sulphur flower, we get sodium thiosulphate.

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

(vi) On heating KBr with orthophosphoric acid, we get hydrobromic acid.

$$3KBr + H_3PO_4 \longrightarrow 3HBr + K_3PO_4$$

(vii) By heating solution of potassium chlorate with I2 and Cl2 is liberated.

$$2KClO_3 + I_2 \longrightarrow 2KlO_3 + Cl_2$$

Note: It is the only reaction in which Cl2 is displaced by iodine.

(viii) On heating nitre with Zn in presence of aqueous NaOH, reduction of nitre to ammonia takes place.

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + 2[H]$$
  
 $KNO_3 + 8[H] \longrightarrow KOH + 2H_2O + NH_3$ 

(ix) Conversion of nitre into nitric oxide involves the following steps:

$$[KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3] \times 2$$

$$2HNO_3 \longrightarrow H_2O + 2NO + 3[O]$$

$$[2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 3$$

$$2KNO_3 + 6FeSO_4 + 5H_2SO_4 \longrightarrow 2KHSO_4 + 3Fe_2(SO_4)_3$$

$$+ 4H_2O + 2NO_4$$

(x) Thermal decomposition of nitre gives oxygen.  $2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2$ 

$$2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2$$

- Q. 2. How will you obtain:
  - (i) Silver from silver coin.
  - (ii) Silver oxide from silver nitrate.
  - (iii) Silver from silver sulphide.
  - (iv) Silver chloride from silver.
  - (v) Copper from copper sulphate.
  - (vi) Cupric chloride from cuprous carbonate.
  - (vii) Cuprous chloride from cupric chloride.
  - (viii) Cuprous chloride from copper sulphate.
  - (ix) Cuprous oxide from copper sulphate.
- (i) When silver coin is dissolved in HNO3, both Ag and Cu Ans. form their nitrates.

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + 2H_2O + NO\uparrow$$
  
 $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO\uparrow$   
Iding HCl to the solution, white precipitate of AgCl

On adding HCl to the solution, white precipitate of AgCl is formed.

$$\begin{array}{c} AgNO_3 + HCl \longrightarrow AgCl \downarrow + HNO_3 \\ (White ppt.) \end{array}$$

AgCl is reduced to metallic silver by zinc dust and HCl.

$$AgCl + [H] \xrightarrow{(Zn + dil. HCl)} Ag + HCl$$

(ii) Silver nitrate when dissolved in aqueous NaOH gives precipitate of Ag<sub>2</sub>O.

 $2AgNO_3 + 2NaOH \longrightarrow 2NaNO_3 + Ag_2O + H_2O$ 

(iii) We can obtain silver from Ag<sub>2</sub>S by cyanide process.

$$\begin{array}{c} Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S \\ 2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag \end{array}$$

(iv) Ag dissolves in HNO3 to give AgNO3. On adding HCl to AgNO<sub>3</sub>, we get white precipitate of AgCl.

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO + 2H_2O$$

$$AgNO_3 + HCl \longrightarrow AgCl + HNO_3$$
(White ppt.)

(v) By adding iron turnings to aqueous solution of CuSO<sub>4</sub>, we get a deposition of copper metal.

$$CuSO_4 + Fe \longrightarrow Cu + FeSO_4$$

(vi) On adding dil. HCl to copper carbonate, we get cupric chloride.

$$CuCO_3 + 2HCl \longrightarrow CuCl_2 + H_2O + CO_2$$

(vii) 
$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$
  
 $2CuCl_2 + 2[H] \longrightarrow Cu_2Cl_2 + 2HCl_3$ 

(viii) By passing SO<sub>2</sub> gas through the solution of CuSO<sub>4</sub> and NaCl in equimolar mixture, we get white precipitate of cuprous chloride.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$

$$2CuSO_4 + 2NaCl + 2[H] \longrightarrow Cu_2Cl_2 + 2NaHSO_4$$
(White ppt.)

(ix) When aqueous solution of CuSO<sub>4</sub> is heated with NaOH and glucose, we get brown precipitate of cuprous oxide.

$$\begin{array}{c} \text{CuSO}_4 + 2\text{NaOH} \longrightarrow \text{Cu(OH)}_2 + \text{Na}_2\text{SO}_4 \\ 2\text{Cu(OH)}_2 \longrightarrow \text{Cu}_2\text{O} + 2\text{H}_2\text{O} + [\text{O}] \\ \text{C}_6\text{H}_{12}\text{O}_6 + [\text{O}] \longrightarrow \text{C}_6\text{H}_{12}\text{O}_7 \\ \text{Gluconic acid} \end{array}$$

- Q. 3. Bring out the following interconversions:
  - (a) Carbon monoxide into carbon.
  - (b) Carbon dioxide to carbon.
  - (c) Carbon monoxide from water gas.
  - (d) Red lead to litharge.
  - (e) Lead to red lead.
  - (f) Litharge to red lead.

(a) By passing CO through red hot CuO, it is converted to carbon Ans. dioxide.

$$CuO + CO \longrightarrow Cu + CO_2$$

When burning magnesium ribbon is placed in a gas jar of CO<sub>2</sub>, we get carbon.

$$2Mg + CO_2 \longrightarrow 2MgO + C$$

- (b) See above part.
- (c) By passing water gas over nickel, CO combines to nickel carbonyl.

$$Ni + 4[CO + H_2] \longrightarrow Ni(CO)_4 + 4H_2\uparrow$$

Decomposition of nickel carbonyl gives CO(g).

$$Ni(CO)_4 \xrightarrow{200^{\circ}C} Ni + 4CO^{\uparrow}$$

(d) By heating red lead at 470°C, we get litharge.

$$\begin{array}{ccc}
2\text{Pb}_3\text{O}_4 & \xrightarrow{470^{\circ}\text{C}} & \text{6PbO} + \text{O}_2 \\
\text{Red lead} & & \text{Litharge}
\end{array}$$

(e) By heating metallic lead in air, oxidation takes place to give red lead.

$$\begin{array}{c} \text{2Pb + O}_2 \longrightarrow \text{2PbO} \\ \text{6PbO + O}_2 \xrightarrow{340^{\circ}\text{C}} \text{2Pb}_3\text{O}_4 \\ \text{Red lead} \end{array}$$

(f) Litharge on heating in air at a high temperature (340°C) gives red lead.

- Q. 4. How will you obtain:
  - (a) Microcosmic salt from disodium hydrogen phosphate.
  - (b) Sodium metaphosphate from microcosmic salt.
  - (c) Barium nitrate from barium sulphate.
  - (d) Barium chloride from barium nitrate.
  - (e) Barium chloride from barium sulphate.
  - (f) Bleaching powder from lime.
  - (g) Quicklime from calcium chloride.
  - (h) Zinc nitrate from zinc chloride.
  - Anhydrous magnesium chloride from magnesium sulphate.
  - (i) Zinc sulphide from zinc chloride.
  - (k) Calomel from mercury.
  - (1) Corrosive sublimate from calomel.
  - (m) Mercury from calomel.
  - (n) Calomel from corrosive sublimate.
- Equal amounts of ammonium chloride and disodium hydrogen Ans. phosphate are dissolved in hot water. On crystallisation, crystals of microcosmic salt are obtained.

$$Na_2HPO_4 + NH_4Cl \longrightarrow NaNH_4HPO_4 + NaCl$$

$$\downarrow^{4H_2O}$$

$$NaNH_4HPO_4 \cdot 4H_2O$$

Microcosmic salt

(b) On heating microcosmic salt, sodium metaphosphate is

$$NaNH_4HPO_4 \cdot 4H_2O \xrightarrow{\Delta} NaPO_3 + NH_3 + 5H_2O$$

(c) Barium sulphate is heated with carbon to get barium sulphide. This is dissolved in dilute HNO3 and the solution is put to crystallisation.

$$BaSO_4 + 4C \longrightarrow BaS + 4CO$$
  
 $BaS + 2HNO_3 \longrightarrow Ba(NO_3)_2 + H_2S$ 

(d) Barium carbonate is first precipitated by adding ammonium carbonate solution to barium nitrate solution. The precipitate is then dissolved in dilute HCl and solution is crystallised to get crystals of barium chloride.

$$Ba(NO_3)_2 + (NH_4)_2CO_3 \longrightarrow BaCO_3 + 2NH_4NO_3$$

$$BaCO_3 + 2HCI \longrightarrow BaCl_2 + H_2O + CO_2$$

 $BaSO_4 + 4C \longrightarrow BaS + 4CO$ 

BaS is dissolved in dilute HCl and the solution is crystallised to get BaCl2 crystals.

(f) Lime is treated with water to get Ca(OH)2. On passing Cl2 over dry Ca(OH)2, bleaching powder is formed.

$$\begin{array}{c} \text{CaO} + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 \\ \text{Ca(OH)}_2 + \text{Cl}_2 \longrightarrow \text{CaOCl}_2 + \text{H}_2\text{O} \end{array}$$

(g) Calcium chloride is dissolved in water. Ammonium carbonate is added to precipitate calcium carbonate. The precipitate on strong heating gives quicklime.

CaCl<sub>2</sub> + (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> 
$$\longrightarrow$$
 CaCO<sub>3</sub> + 2NH<sub>4</sub>Cl
$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

(h) Zinc chloride solution is treated with sodium bicarbonate solution when zinc carbonate gets precipitated. The precipitate is dissolved in dilute HNO3 and the solution is crystallised to get crystals of zinc nitrate.

$$ZnCl_2 + 2NaHCO_3 \longrightarrow ZnCO_3 + 2NaCl + H_2O + CO_2$$
  
 $ZnCO_3 + 2HNO_3 \longrightarrow Zn(NO_3)_2 + H_2O + CO_2$ 

(i) Magnesium sulphate solution is treated with sodium bicarbonate solution when magnesium carbonate gets precipitated.

$$MgSO_4 + 2NaHCO_3 \longrightarrow MgCO_3 + Na_2SO_4 + H_2CO_3$$

+ H<sub>2</sub>O +CO<sub>2</sub>

The precipitate is dissolved in small quantity of dilute HCl. The solution is concentrated and treated with conc. NH<sub>4</sub>Cl solution. On evaporation, a double salt MgCl<sub>2</sub>·NH<sub>4</sub>Cl·6H<sub>2</sub>O is formed. The crystals on heating give anhydrous MgCl<sub>2</sub>.

$$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2$$

$$MgCl_2 + NH_4Cl + 6H_2O \longrightarrow MgCl_2 \cdot NH_4Cl \cdot 6H_2O$$

$$MgCl_2\cdot NH_4Cl\cdot 6H_2O \longrightarrow MgCl_2 + NH_3 + HCl + 6H_2O$$

(j) ZnCl2 is dissolved in water. NH4Cl and NH4OH are added to solution and H2S gas is passed. ZnS gets precipitated which is filtered.

$$ZnCl_2 + 2NH_4OH + H_2S \longrightarrow ZnS + 2NH_4Cl + 2H_2O$$

(k) Mercury is dissolved in conc. H<sub>2</sub>SO<sub>4</sub> and the solution is evaporated to get solid HgSO<sub>4</sub>. The solid is grinded with NaCl and Hg and the mixture is heated. Mercurous chloride sublimes and collected.

$$Hg + 2H_2SO_4 \longrightarrow HgSO_4 + SO_2 + 2H_2O$$
  
 $HgSO_4 + 2NaCl + Hg \longrightarrow Hg_2Cl_2 + Na_2SO_4$ 

(1) Calomel is dissolved in aqua-regia and the solution is put to crystallisation when crystals of corrosive sublimate are obtained.

$$HNO_3 + 3HCl \longrightarrow NOCl + 2Cl + 2H_2O$$
  
 $Hg_2Cl_2 + 2Cl \longrightarrow 2HgCl_2$ 

(m) Hg<sub>2</sub>Cl<sub>2</sub> solution is reduced by stannous chloride solution into mercury.

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

(n) Calomel is obtained by passing sulphur dioxide through the solution of mercuric chloride.

$$2HgCl_2 + 2H_2O + SO_2 \longrightarrow Hg_2Cl_2 + H_2SO_4 + 2HCl$$

- O. 5. Show by balanced equations how would you obtain from HNO3:
  - (a) NO, (b) NO<sub>2</sub>, (c)  $N_2O$ ,

 $S + 2HNO_3(conc.) \longrightarrow H_2SO_4 + 2NO\uparrow$ (a) Ans.

(b) 
$$C + 4HNO_3(conc.) \longrightarrow CO_2 \uparrow + 4NO_2 \uparrow + 2H_2O$$

- $4Cu + 10HNO_3(dil.) \longrightarrow 4Cu(NO_3)_2 + 5H_2O + N_2O\uparrow$
- (d)  $5Cu(red hot) + 2HNO_3(conc.) \longrightarrow 5CuO + N_2 \uparrow + H_2O$
- Q. 6. Give the chemical equations for synthesis of the following
- compounds using corresponding elemental halogen:
  - (d) KBrO<sub>3</sub>, (a)  $Br_2O$ , (b)  $BrO_3$ , (c)  $OF_2$ ,
  - (f) Cl<sub>2</sub>O, (g)  $I_2O_5$ , (h)  $HClO_4$ .
- $2Br_2 + HgO \longrightarrow Br_2O + HgBr_2$ Ans.

(b) 
$$\frac{1}{2}Br_2 + O_3 \xrightarrow{0^{\circ}C} BrO_3$$

(c) 
$$2F_2 + 2NaOH \longrightarrow 2NaF + OF_2 + H_2O$$

- (d)  $3Br_2 + 6KOH \longrightarrow 5KBr + KBrO_3 + 3H_2O$
- (e)  $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

$$2H^{+} + 2ClO_{3}^{-} + \begin{matrix} COOH \\ COOH \end{matrix} \longrightarrow 2ClO_{2} + 2CO_{2} + 2H_{2}O$$

- $2Cl_2 + HgO \longrightarrow Cl_2O + HgCl_2$ (f)
- $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

 $\begin{array}{ccc} & 2HIO_3 \longrightarrow & H_2O \,+\, I_2O_5 \\ \text{(h)} & 3Cl_2 \,+\, 6NaOH \longrightarrow & 5NaCl \,+\, NaClO_3 \,+\, 3H_2O \end{array}$ 

$$4\text{NaClO}_3 \xrightarrow{\Delta} \text{NaCl} + 3\text{NaClO}_4$$

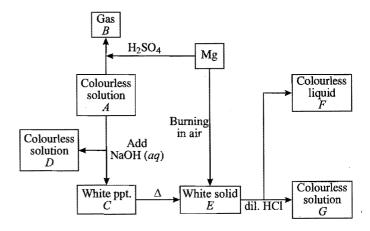
Q.7. How would you obtain pure copper oxide from brass?

Ans. Brass (containing Cu and Zn) 
$$\bigcirc$$
 Conc. HNO<sub>3</sub>  $[Cu(NO_3)_2 + Zn(NO_3)_2]$ 

Blue coloured precipitate of Cu(OH)2

CuO (Cupric oxide)

Q. 8. Identify 'A' to 'G' in the following road map diagram. Explain the reactions involved.



**Ans.** (A):  $MgSO_4$ , (B):  $H_2$ , (C):  $Mg(OH)_2$ , (D):  $Na_2SO_4$ , (E): MgO, (F): water, (G): MgCl<sub>2</sub>.

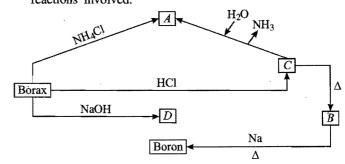
$$\begin{array}{c} \text{Mg} + \text{H}_2\text{SO}_4 & \longrightarrow & \text{MgSO}_4 + \text{H}_2 \uparrow \\ & [A] & [B] \end{array}$$

$$\begin{array}{c} \text{MgSO}_4 + 2\text{NaOH} & \longrightarrow & \text{Mg(OH)}_2 + \text{Na}_2\text{SO}_4 \\ & [C] & [D] \end{array}$$

$$\begin{array}{c} \text{Mg(OH)}_2 & \stackrel{\Delta}{\longrightarrow} & \text{MgO} \\ & [E] \end{array}$$

$$\text{MgO} + 2\text{HCI} & \longrightarrow & \text{MgCl}_2 + \text{H}_2\text{O} \end{array}$$

Q. 9. Properties of borax are represented by the following road map. Identify the compounds 'A' to 'D' and explain the reactions involved.



**Ans.** (A): BN, (B):  $B_2O_3$ , (C):  $H_3BO_3$ , (D):  $NaBO_2$ . Reactions involved are:

$$Na_2B_4O_7 + 4NH_4C1 \longrightarrow 4BN + 2NaC1 + 7H_2O + 2HC1$$

$$[A]$$
 $BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$ 

$$[C]$$

$$\begin{array}{c} \text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} \longrightarrow 4\text{H}_3\text{BO}_3 + 2\text{NaCl} \\ \text{Na}_2\text{B}_4\text{O}_7 + 4\text{NaOH} \longrightarrow 8\text{NaBO}_2 + 2\text{H}_2\text{O} \\ 2\text{H}_3\text{BO}_3 \stackrel{\Delta}{\longrightarrow} \text{B}_2\text{O}_3 + 3\text{H}_2\text{O} \\ & \text{B}_2\text{O}_3 + 6\text{Na} \stackrel{\Delta}{\longrightarrow} 2\text{B} + 3\text{Na}_2\text{O} \end{array}$$

Q.10. Complete the following road map:

$$H_2C_2O_4 \xrightarrow{\text{Conc.} H_2SO_4} (A) + (B) + (C)$$
 $Gas Gas Liquio$ 

Gas (A) burns with blue flame and converts nickel into a gas.

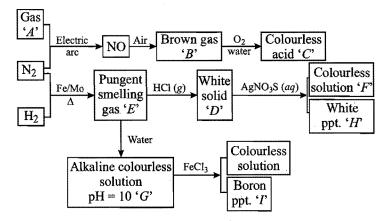
Gas (B) turns lime water milky. Liquid (C) produces blue colour when comes in contact with anhydrous copper sulphate.

$$(A) + \operatorname{Cl}_2 \longrightarrow (D) \xrightarrow{\operatorname{NH}_3} (E)$$

$$(B) \xrightarrow{\operatorname{NH}_3} \xrightarrow{\operatorname{Heat}}$$

**Ans.** (A):CO, (B):CO<sub>2</sub>, (C):H<sub>2</sub>O, (D):COCl<sub>2</sub>, (E):NH<sub>2</sub>CONH<sub>2</sub>.

**Q.11.** Identify the missing chemicals 'A' to T.



**Ans.**  $(A): O_2, (B): NO_2, (C): HNO_3, (D): NH_4Cl, (E): NH_3,$ 

 $(F): NH_4NO_3, (G): NH_4OH, (H): AgCl, (I): Fe(OH)_3.$ 

#### Q.12. How will you obtain:

- (a) Anhydrous aluminium chloride from alumina.
- (b) Aluminium sulphate from common alum.
- (c) Ammonium sulphate from ammonium chloride.
- (d) Phosphorus from bone ash.
- (e) Orthophosphoric acid (pyrophosphoric acid/metaphosphoric acid) from phosphorus.
- (f) Sulphur from  $H_2S$  or  $SO_2$ .
- (g) HBr from bromine.
- (h) Ferric sulphate from ferrous sulphate.
- (i) Ferric chloride from ferrous sulphate.
- (i) Ferrous sulphate from Mohr's salt.

Ans. (a) By heating a mixture of alumina and carbon in an atmosphere of chlorine, anhydrous aluminium chloride is obtained.

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$$
 $Vapours$ 
 $Cooled$  Solid

(b) NH<sub>4</sub>OH is added to alum solution when aluminium hydroxide gets precipitated. The precipitate is dissolved in dilute H<sub>2</sub>SO<sub>4</sub>. The solution on crystallisation gives crystals of aluminium sulphate.

- (c) Ammonium chloride is treated with NaOH. NH<sub>3</sub> is evolved which is absorbed in dilute H<sub>2</sub>SO<sub>4</sub>. The solution on evaporation gives crystals of ammonium sulphate.
- (d) Bone ash on heating with coke and sand in an electric furnace at 1500°C gives vapours of phosphorus which are condensed in water.

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \longrightarrow 3CaSiO_3 + 2P + 5CO$$

(e) Phosphorus on heating with conc. HNO<sub>3</sub> forms orthophosphoric acid. Orthophosphoric acid when heated at specific temperature forms other oxy acids.

(f) H<sub>2</sub>S by oxidation gives sulphur.

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$
  
 $H_2S + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + S$ 

On burning magnesium in SO2, S is obtained.

$$2Mg + SO_2 \longrightarrow 2MgO + S$$

$$\downarrow HCI$$

$$MgCl_2 \text{ (soluble)}$$
 $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$ 

(g) Bromine combines with red phosphorus kept in water.

$$2P + 3Br_2 \longrightarrow 2PBr_3$$

Phosphorus bromide immediately undergoes hydrolysis giving HBr.

$$PBr_3 + 3H_2O \longrightarrow H_3PO_3 + 3HBr$$

(h) Ferrous sulphate is heated with concentrated sulphuric acid. The solution on concentration gives ferric sulphate crystals.

$$\frac{\text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{O} + \text{SO}_2 + [\text{O}]}{2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + [\text{O}] \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}}{2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2 + 2\text{H}_2\text{O}}$$

(i) Ferrous sulphate is first converted into ferric sulphate. Ammonium hydroxide is added to ferric sulphate solution when a brown precipitate of ferric hydroxide is obtained. The precipitate is dissolved in dilute HCl and the solution on crystallisation gives ferric chloride crystals.

$$Fe_2(SO_4)_3 + 6NH_4OH \longrightarrow 2Fe(OH)_3 + 3(NH_4)_2SO_4$$

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

(j) Mohr's salt solution is treated with NaOH solution. A precipitate of ferrous hydroxide is formed. The precipitate is dissolved in dilute  $\rm H_2SO_4$  and the solution is put to crystallisation when crystals of ferrous sulphate are obtained.

$$\begin{split} \text{FeSO}_4 \cdot (\text{NH}_4)_2 &\text{SO}_4 \cdot 6\text{H}_2\text{O} + 2\text{NaOH} \longrightarrow &\text{Fe}(\text{OH})_2 \\ &+ \text{Na}_2 \text{SO}_4 + (\text{NH}_4)_2 \text{SO}_4 + 6\text{H}_2\text{O} \\ \text{Fe}(\text{OH})_2 + \text{H}_2 \text{SO}_4 \longrightarrow &\text{FeSO}_4 + 2\dot{\text{H}}_2\text{O} \end{split}$$

Q.13. Identify the following:

$$Na_2CO_3 \xrightarrow{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow{S} C \xrightarrow{I_2} D$$

[HT 2003]

$$\begin{array}{c} \text{Na}_2\text{CO}_3 + 2\text{SO}_2 + \text{H}_2\text{O} \longrightarrow 2\text{NaHSO}_3 + \text{CO}_2 \\ \text{2NaHSO}_3 + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{CO}_2 \\ \text{(B)} \\ \text{Na}_2\text{SO}_3 + \text{S} \longrightarrow \text{Na}_2\text{S}_2\text{O}_3 \text{ (Hypo)} \\ \text{(C)} \\ \text{2Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \\ \text{(D)} \end{array}$$

Q.14. Identify the following:

$$Si + CH_3Cl \xrightarrow{Cu \text{ powder} \atop 570 \text{ K}} (A) \xrightarrow{H_2O} (B) \xrightarrow{Polymerisation} Silicon$$

$$\downarrow O_2$$

(C) 
$$\xrightarrow{\text{Excess of coke}}$$
 (D)

Ans. Si + 2CH<sub>3</sub>Cl 
$$\xrightarrow{\text{Cu powder}}$$
 (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>
(A)

Polymeri- $(CH_3)_2SiCl_2 + H_2O \longrightarrow (CH_3)_2Si(OH)_2 \xrightarrow{sation} Silicon$ (B) Dimethyl silandiol

$$Si + O_2 \xrightarrow{Burns} SiO_2$$
(C)

$$SiO_2 + 3C \xrightarrow{Arc} SiC + 2CO$$

$$Carborundum$$

**Q.15.** On the basis of following reactions, identify (A), (B), (C)and (D) and write down their chemical formulae.

(i) 
$$(A) + Zn \xrightarrow{\text{Heat}} (B)$$
 gas

(ii) 
$$(A) + (C) \xrightarrow{\text{Heat}} PH_3$$

(iii) 
$$(A) + NH_4Cl \xrightarrow{Heat} (D)$$
 gas

(i) (A) is sodium hydroxide.

$$2NaOH + Zn \longrightarrow Na_2ZnO_2 + H_2$$
(B)

(ii) (C) is phosphorus.

$$3NaOH + 4P + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$$

(iii) (D) is ammonia gas.

$$NH_4Cl + NaOH \longrightarrow NH_3 + NaCl + H_2O$$

Q.16. Explain the following reactions:

(a) Metal (M) 
$$\xrightarrow{\text{Dissolves}}$$
 Pale green soln.  $\xrightarrow{\text{Add}}$ 

Whitish precipitate quickly turning brown  $\xrightarrow{HCl}$ 

dissolves giving yellow soln.

(b) Black substance 
$$\xrightarrow{\text{Heated in} \atop \text{air with Na}_2\text{CO}_3}$$
 dark mass  $\xrightarrow{\text{Extracted} \atop \text{with water}}$  green soln.  $\xrightarrow{\text{Chlorine} \atop \text{Water}}$  pink soln.

Ans. (a) Metal (M) is iron. Fe + 
$$H_2SO_4 \longrightarrow FeSO_4$$
,  
 $FeSO_4 + NaOH \longrightarrow Fe(OH)_2 \longrightarrow Fe(OH)_3 \xrightarrow{HCl} FeCl_3$   
Yellow soln.

(b) 
$$MnO_2 + Na_2CO_3 + O_2 \xrightarrow{H_2O} Na_2MnO_4 \xrightarrow{Cl_2} NaMnO_4$$
Black
Black
Substance

Green soln.

Pink soln.

#### TYPE 2: Matching of Columns

#### Set 1

- (A) (X) (i) Green vitriol
  - (ii) Blue vitriol (iii) White vitriol

  - (iv) Glauber's salt
  - (v) Oil of vitriol
  - (vi) Mohr's salt
- (vii) Sindri fertilizer
- (viii) Gypsum
  - (ix) Epsom salt
  - (x) Barytes
- - (i) Lepidolite
  - (ii) Beryl (iii) Colemanite
  - (iv) Cryolite
  - (v) Cinnabar
  - (vi) Carnallite
  - (vii) Calamine
- (viii) Malachite
  - (ix) Galena
  - (x) Cassiterite
- (C)
  - (i) Washing soda
  - (ii) Baking soda
  - (iii) Litharge
  - (iv) Red lead
  - (v) Lunar caustic
- (vi) Oxone
  - (vii) Philosopher's wool
  - (viii) Spinel
  - (ix) Calomel
  - (x) Corrosive sublimate
- - (i) Bosch's process
  - (ii) Castner-Kellner cell
  - (iii) Solvay's process
  - (iv) Deacon's process
  - (v) Parke's process
  - (vi) Contact process
  - (vii) Retort process
- (viii) Dennis method
- (ix) Carter's process
- (x) Open-hearth's process

- **(Y)**
- (a) Ferrous sulphate
- (b) Ammonium sulphate
- (c) Sulphuric acid
- (d) Barium sulphate
- (e) Zinc sulphate
- (f) Calcium sulphate
- (g) Magnesium sulphate
- (h) Sodium sulphate
- (i) Ferrous ammonium sulphate
- (i) Copper sulphate
- (a) Na<sub>3</sub>AlF<sub>6</sub>
- (b) ZnCO<sub>3</sub>
- (c) PbS
- (d) CuCO<sub>3</sub>·Cu(OH)<sub>2</sub>
- (e) 3BeO·Al<sub>2</sub>O<sub>3</sub>·6SiO<sub>2</sub>
- (f)  $SnO_2$
- (g)  $Ca_2B_6O_{11}.5H_2O$
- (h) HgS
- (i) (Li, Na, K)<sub>2</sub>Al<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub>(F,OH)<sub>2</sub>
- (j) KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O
- (a) AgNO<sub>3</sub>
- (b) MgAl<sub>2</sub>O<sub>4</sub>
- (c) Na<sub>2</sub>O<sub>2</sub>
- (d) ZnO
- (e) PbO
- (f) Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O
- (g) NaHCO<sub>3</sub>
- (h)  $Pb_3O_4$
- (i) Hg<sub>2</sub>Cl<sub>2</sub>
- (i) HgCl<sub>2</sub>
- (a) Isolation of fluorine
- (b) Manufacture of silver
- (c) Manufacture of sulphuric acid
- (d) Manufacture of white lead
- (e) Manufacture of phosphorus
- (f) Manufacture of chlorine
- \*(g) Manufacture of hydrogen
- (h) Manufacture of wrought iron
- Manufacture of caustic soda
- (i) Manufacture of sodium bicarbonate

#### Set 2

#### (A) **(X)** (i) Constantan (ii) Brass (iii) Rolled gold

**(Y)** (a) Cu, Al

- $(\mathbf{Z})$ (l) Measuring tapes
- (b) Fe,Cr, Ni
- (m) Domestic utensils
- (iv) Invar
- (c) Pb, Sn, Sb (d) Cu, Ni
- (n) Common articles
- (v) Stainless steel
- (e) Pb, Sn (f) Al, Mg
- (p) Airships (q) Printing types

(o) Soldering

(vii) Type metal

(vi) Solder

- (g) Fe, Ni
- (r) Artificial jewellery

- (viii) Magnalium
- (h) Cu, Zn
- (s) Electrical resistances

- (i) Water gas
  - (ii) Producer gas
- (a)  $N_2O$ (b) NH<sub>2</sub>NH<sub>2</sub>
- (l) Fuel gas (m) Basic flux
- (c) A dilute (iii) Laughing gas solution
- (n) Manufacture of hydrogen

- (iv) Hydrazine
- (d) CaO
- (o) Fertilizer

- (v) Perhydrol
- (e)  $CaCN_2 + C$ (p) Antiseptic and
- (vi) Quicklime
- (f)  $CO + N_2$

of H<sub>2</sub>O<sub>2</sub>

germicide (q) Rocket fuel with

- (vii) Nitrolim
- (g) SiC
- $H_2O_2$ (r) Abrasive
- (viii) Carborundum
- (h)  $CO + H_2$
- (s) Anaesthetic in nature

#### Set 3

#### (A) Match the following:

#### Column I

#### Column II

- (i)  $Sb^{3+} \longrightarrow (SbO)^{+}$
- (a) Acidification
- (ii)  $(CrO_4^{2-}) \longrightarrow (Cr_2O_7^{2-})$
- (b) Heat
- (iii)  $(MnO_4^2) \longrightarrow (MnO_4^-)$
- (c) Hydrolysis
- (iv)  $(B_4O_7^2) \longrightarrow [B(OH)_3]$
- (d) Oxidation
- (B) Match the extraction process listed in column I with metals listed in column  $\Pi$ :

#### Column I

#### Column II

- (i) Electrolytic reduction
- (a) Lead
- (ii) Self reduction
- (b) Aluminium
- (iii) Leaching
- (c) Silver
- (iv) Carbon reduction
- (d) Magnesium
- Match the colour listed in column I with compounds listed in column II:

#### Column I

#### Column II

(i) Yellow

- (a) KMnO<sub>4</sub>
- (ii) Colourless
- (b) PbI<sub>2</sub>

(iii) Purple

(c) CuSO<sub>4</sub>

(iv) Black

- (d) K2CrO4 (e) PbS
- (D) Match the following:

#### Column I

#### Column II

- (i) Copper
- (ii) Zinc

- (iii) Tin
- (iv) Nickel

- (a) Brass (b) Bronze
- (c) Invar
- (d) German silver

(E) Match the following:

#### Column I

#### Column II

- (i) Ammonium nitrate
- (a) Fertilizer
- (ii) Superphosphate of lime
- (b) Purgative (c) Explosive
- (iii) Mercurous chloride (iv) Sodium thiosulphate
- (d) Photography
- (v) Silver bromide
- (e) Antichlor
- (F) Match the extraction processes listed in column I with metals listed in column II: [I.I.T. 2006]

#### Column I

#### Column II

- (a) Self reduction
- (b) Carbon reduction
- (p) Lead (q) Silver
- (c) Complex formation and displacement by metal
- (d) Decomposition of iodide
- (s) Boron

(r) Copper

(G) Match the following:

#### .[I.I.T. 2006]

#### Column I

#### (a) $Bi^{3+} \longrightarrow (BiO)^{+}$

- (p) Heat
- (b)  $[AlO_2]^+ \longrightarrow Al(OH)_3$
- (q) Hydrolysis (r) Acidification

Column II

- (c)  $SiO_4^{4-} \longrightarrow Si_2O_7^{6-}$ (d)  $(B_4O_7)^{2-} \longrightarrow [B(OH)_3]$
- (s) Dilution by water
- (H) Match the reactions in column I with nature of reaction/type of the products in column  $\Pi$ . [I.I.T. 2007]

#### Column I

#### Column II

- (a)  $O_2^- \longrightarrow O_2 + O_2^{2-}$ (b)  $CrO_4^- + H^+ \longrightarrow$
- (p) Redox reaction (q) One of the products has
- (c)  $MnO_4^- + NO_2 + H^+ \longrightarrow$
- trigonal planar structure (r) Dimeric bridged

tetrahedral metal ion

(d)  $NO_3^- + H_2SO_4 + Fe^{2+} \longrightarrow$  (s) Disproportionation

### **ANSWERS**

#### Matching of Columns

#### Set 1

- (A) (i-a) (ii-j) (iii-e) (iv-h) (v-c) (vi-i) (vii-b) (viii-f) (ix-g)(x-d)
- (B) (i-i) (ii-e) (iii-g) (iv-a) (v-h) (vi-j) (vii-b) (viii-d)(ix--c)(x-f)
- (C) (i—f) (ii—g) (iii—e) (iv—h) (v—a) (vi—c) (vii—d) (viii—b) (ix-i)(x-j)
- (D) (i-g) (ii-i) (iii-j) (iv-f) (v-b) (vi-c) (vii-e) (viii-a) (ix-d)(x-h)
- Set 2 (A) (i - d - s) (ii - h - m)
  - (iii—a—r) (vi-e-o) (vii-c-q) (viii-f-p)
    - (iv—b—q)
  - (ii—f—l) (B) (i—h—n) (iii—a—s) (vi-d-m) (vii-e-o) (viii-g-r)
- Set 3

(A) (i—c)

(B) (i—b, d)

- (ii—a) (ii-a)
- (iii—d)
- (iii—b, c) (iv--a)

(1	C) (i—b, d) (ii—c) (iii—a) (iv—e) D) (i—a, b, d) (ii—a, d) (iii—d) (iv—c, d) C) (i a a) (iii b) (iv d a) (v d)		14.	Which does not give oxygen on heating?  (a) $KMnO_4$ $\square$ (b) $(NH_4)_2Cr_2O_7$ $\square$ (c) $KClO_3$ $\square$ (d) $HgO$	
	E) (i—a, c) (ii—a) (iii—b) (iv—d, e) (v—d) F) (a—p, r) (b—p, r) (c—q) (d—s)		15.	An interhalogen compound is:	٠ ـ
	$G) (a-q) \qquad (b-r) \qquad (c-p) \qquad (d-r, q)$	ı		(a) $\overline{1_3}$ $\Box$ (b) $(CN)_2$ $\Box$	]
	H(a-p, s) $(b-r)$ $(c-p, q)$ $(d-p)$		,	(c) $BrF_3$ $\Box$ (d) $N_3H$	j
	( 1) ( 1) ( 1)	- 1	16.	Which is soluble in ammonia?	_
TYF	PE 3: Multiple Choice—A	- 1		(a) $Cu(OH)_2$ $\Box$ (b) $Cr(OH)_3$	<u>.</u>
	•	- 1		(c) $Fe(OH)_3$ $\Box$ (d) $Al(OH)_3$	
	n each of the following only one answer is correct. Select the	ie	17.	A magnetic moment of 1.41 B.M. will be shown by one among	g.
corre	ect one.	- 1		the following compounds:	<i>D</i>
Set	<b>1</b> \	- 1			7
1.	Nitrogen dioxide cannot be obtained by heating:	- 1		(a) $[Cu(NH_3)_4]^{2+}$	
		⊐			
		<u>-</u> 1		[Hint: The magnetic moment = $\sqrt{n(n+1)}$ = 1.41, i.e., $n = 1$ . In	n
2.	The catalyst used in the manufacture of sulphuric acid t	_ 1		complex [Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> , Cu <sup>2+</sup> ion has one unpaired orbital.	
	contact process is:	~ I	18.	XeF <sub>6</sub> on complete hydrolysis gives:	
			10.	(a) $XeO_3$ $\square$ (b) $XeOF_4$	٦
		5		· · · · · · · · · · · · · · · · · · ·	7
3	The element with highest first ionisation potential is:	-	19.	Which of the following is not a double salt but a complete	_
٦.		_	1,	salt?	A.
				(a) KCl·MgCl <sub>2</sub> ·6H <sub>2</sub> O	٦.
1	Among the following the molecule, that is linear, is:	- 1			_
٠,					_
			20.	Which one of the following compounds has the smalles	
5.	Which of the following will not produce a precipitate wi	- 1	20.	bond angle in its molecule?	<b>,</b> ,
٠,	dilute silver nitrate solution?	· 1			<b>_</b>
	2 2				_
		5	21.	The pair of species having identical shapes for molecules of	_
6.	The compound that is not a Lewis acid is:	_	21.	both species is:	<i>/</i> 1
o.	<u>-</u>				
	· · · · · · · · · · · · · · · · · · ·	- 1			_
7	An alloy, which does not contain copper, is:	_	22.	A red solid is insoluble in water. However, it becomes solu	
	, ,	╗╏	Bal And 4	ble if some KI is added to water. Heating the red solid in	
	· ·			test tube results in the liberation of some coloured viole	
8.	The metal, which does not form amphoteric oxide, is:	- 1		fumes and droplets of a metal appear on the cooler parts of	
0.				the test tube. The red solid is:	/1
	* *				
Q	In which complex ion is the metal in zero oxidation state?	- 4			<u> </u>
٦.	. 2	o l	23.	Borax can be converted to boron by the following steps:	
	2	<u>-</u> 1	<i></i>	<del>-</del> -	
10		1		Borax $\xrightarrow{\cdot A'}$ $H_3BO_3$ $\xrightarrow{\text{Heat}}$ $B_2O_3$ $\xrightarrow{\cdot B'}$ Boron, the	ıe
10.	The oxide that gives hydrogen peroxide on treatment will dilute acid is:	ui j		reagents 'A' and 'B' are:	
		_		(a) acid, Al	
	· · · · · · · · · · · · · · · · · · ·			(c) acid, Fe	
11	(c) MnO <sub>2</sub>	_	24.	0.2 g sample of H <sub>2</sub> O <sub>2</sub> required 10 mL of N KMnO <sub>4</sub> in	a
. 11.				titration in the presence of H <sub>2</sub> SO <sub>4</sub> . The purity of H <sub>2</sub> O <sub>2</sub> is:	
				(a) 25%	
12.		_		= (4) 32 %	
12.			25.	0.7 g of a sample of Na <sub>2</sub> CO <sub>3</sub> ·xH <sub>2</sub> O were dissolved in water	er
				and the volume made up to 100 mL. 20 mL of this solution	
13	The stable compounds in + 1 oxidation state are formed by			required 19.8 mL of 0.1 NHCl for complete neutralization. The	ne
1.0,	(a) B	'y.		value of x is:	
				(-)	
	_ (0) 50	_		(c) $\sim 4$ $\square$ (d) $\sim 1$	
		1	I		

26.	Which one of the following oxides is expected to exhibit	$\Delta_i H_3 \ 1100 \ \text{kJ mol}^{-1}$
	paramagnetic behaviour? [C.B.S.E. (P.M.T.) 2005]	$\Delta_i H_4 1500 \text{ kJ mol}^{-1}$
	(a) $CO_2$ $\square$ (b) $CIO_2$ $\square$	$\Delta_i H_5$ 3200 kJ mol <sup>-1</sup>
	(c) $SO_2$ $\square$ (d) $SiO_2$ $\square$	Find out the number of valence electrons for the element,
27.	The aqueous solution containing which one of the following	'X':
	ions will be colourless? [C.B.S.E. (P.M.T.) 2005]	(a) 4
	(a) $Fe^{2+}$ $\Box$ (b) $Mn^{2+}$ $\Box$	(c) 5
	(c) $Ti^{3+}$	
28.	The complex, [Co(NH <sub>3</sub> ) <sub>4</sub> Br <sub>2</sub> ]Cl can show isomerism:	Set 2
20.	[I.I.T. 2005]	1. In the long form of periodic table, all the non-metals are
	(a) ionisation and geometrical	placed under:
	(b) geometrical and optical	(a) s-block $\Box$ (b) p-block $\Box$
	(c) ionisation and optical (d) only optical	(c) $d$ -block $\Box$ (d) $f$ -block $\Box$
20	O <sub>3</sub> cannot oxidise: [I.I.T. 2005]	2. The elements which exhibit both vertical and horizontal simi-
29.	•	larities are:
	(-)	(a) representative elements
20	(c) $KMnO_4$ $\Box$ (d) $K_2MnO_4$ $\Box$	(b) $p$ -block elements
30.	Which of the following gas is liberated when PbO <sub>2</sub> is reacted	(c) transition elements
	with conc. HNO <sub>3</sub> ? [I.I.T. 2005]	(d) none of the above
	(a) $NO_2$ $\square$ (b) $O_2$ $\square$	3. The shape of a molecule which has 3 bond pairs and one
	(c) NO $\Box$ (d) N <sub>2</sub> O $\Box$	lone pair is:
	$[\text{Hint}: PbO_2 + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O + \frac{1}{2}O_2]$	(a) pyramidal
31.	The incorrect statement among the following is:	(c) triangular planar □ (d) tetrahedral □
	(a) $C_{60}$ is an allotropic form of carbon	4. The radii of F, F, O and O <sup>2-</sup> are in the order of:
	(b) $O_3$ is an allotropic form of oxygen	(a) $O^{2-} > F > F > O$
	(c) $S_8$ is only allotropic form of sulphur $\Box$	(c) $O^{2-} > O > F > F$
	(d) red phosphorus is more stable in air than white	5. The group in which all the elements do not have same
	phosphorus $\square$	number of electrons in their valency shell is:
32.	The pair whose both species are used in anti-acid medicinal	(a) zero $\Box$ (b) second $\Box$
	preparation is:	(c) first $\Box$ (d) seventh $\Box$
	(a) NaHCO <sub>3</sub> and Mg(OH) <sub>2</sub> $\Box$	[Hint: He has two electrons while rest of the members of zero
	(b) $Na_2CO_3$ and $Ca(HCO_3)_2$	group have 8 electrons in the valency shell.]
	(c) $Ca(HCO_3)_2$ and $Mg(OH)_2$	6. The chemical composition of 'slag' formed during the
	(d) $Ca(OH)_2$ and $NaHCO_3$	smelting process in the extraction of copper is:
33.	1 01	(a) $Cu_2O + FeS$ $\Box$ (b) $FeSiO_3$ $\Box$
	matched. The mismatch is:	(c) $CuFeS_2$ $\Box$ (d) $Cu_2S + FeO$ $\Box$
	(a) $[RhCl(PPh_3)_2]$ : hydrogenation	7. When silicon is boiled with caustic soda solution, the gas
	(b) $TiCl_4 + Al(C_2H_5)_3$ : polymerization	evolved is:
	(c) $V_2O_5$ : Haber-Bosch process	(a) $O_2$ $\Box$ (b) $SiH_4$ $\Box$
	(d) nickel: hydrogenation	(c) H <sub>2</sub>
34.	Among the following, the species having square planar	8. Tailing of mercury is a laboratory test for:
	geometry for central atom are:	
	(i) $XeF_4$ (ii) $SF_4$ (iii) $[NiCl_4]^2$ (iv) $[PdCl_4]^2$	
	(a) (i) and (iv)	[Hint: O <sub>3</sub> reacts with Hg to form Hg <sub>2</sub> O which sticks to glass.
	(c) (ii) and (iii) $\Box$ (d) (iii) and (iv) $\Box$	This is called tailing of Hg.]
	[Hint: $XeF_4$ — $sp^3d^2$ hybridization—shape is square planar instead	9. Which alkali metal reacts with nitrogen to form nitride?
	of octahedral due to presence of two lone pairs of electrons on	(a) Cs
	Xe—atom.	(c) K
	SF <sub>4</sub> — $sp^3d$ hybridization—shape is distorted, <i>i.e.</i> , see-saw instead	10. A mixture of Al(OH) <sub>3</sub> and Fe(OH) <sub>3</sub> can be separated easily
	of trigonal bipyramidal due to presence of one lone pair of electrons.	by treating with:
	[NiCl <sub>4</sub> ] <sup>2</sup> — $sp^3$ hybridization—tetrahedral shape	(a) HCl
	[PdCl <sub>4</sub> ] $\stackrel{-}{=}$ hybridization—square planar shape [PdCl <sub>4</sub> ] $\stackrel{2}{=}$ — $dsp^2$ hybridization—square planar shape]	(c) HNO <sub>3</sub>
35.		11. Thermal decomposition of which compound yields a basic
JJ.	are given below:	and acidic oxide simultaneously?
	$\Delta_i H_1 410 \text{ kJ mol}^{-1}$	(a) KClO <sub>3</sub>
	$\Delta_i H_2$ 820 kJ mol <sup>-1</sup>	(c) CaCO <sub>3</sub>
	Little Occ. By High	

12.	Which of the following processes does not involve	a		(a) high atomic mass ☐ (b) d-block (c) f-block ☐ (d) radioactive	
	catalyst?		24.	$[X] + H_2SO_4 \longrightarrow [Y]$ a colourless gas with irritating sm	
	(a) Ostwald's process   (b) Thermite process		24.		
10	(c) Contact process		1	$[Y] + K_2Cr_2O_7 + H_2SO_4 \longrightarrow Green soln. [X] and [Y] are$	
13.	Which of the following shows bond in silicone?		1	(a) $SO_3^{2-}$ , $SO_2$	
			~~	(c) $S^2$ , $H_2S$	Ū
	(a) —Si—C—Si—O—Si—		25.	Mixture $X = 0.02$ mole of [Co(NH <sub>3</sub> ) <sub>5</sub> SO <sub>4</sub> ]Br and 0.02 mole	e of
				[Co(NH <sub>3</sub> ) <sub>5</sub> Br]SO <sub>4</sub> was prepared in 2 litre of solution:	
	(b) Si C Si C Si			1 litre of mixture $X + \text{excess of } AgNO_3 \longrightarrow Y$	
	(b) —Si—C—Si—C—Si—			1 litre of mixture $X + \text{excess of BaCl}_2 \longrightarrow Z$	
				No. of moles of $Y$ and $Z$ are:	_
	(c) —Si—Si—Si—Si—			(a) 0.02, 0.02	
				(c) 0.01, 0.02	
			26.	Chemical compound $(A)$ is used for water softening to rem	
	(d) —Si—O—Si—O—Si—			temporary hardness. Compound (A) reacts with Na <sub>2</sub> CO	_
14	Which compound does not give NH <sub>3</sub> on heating?			give caustic soda. When CO <sub>2</sub> is bubbled through solu-	tion
17.	(a) $(NH_4)_2SO_4$ $\Box$ (b) $(NH_4)_2CO_3$			(A), it turns cloudy. The chemical formula of (A) is:	
	(c) $NH_4NO_2$			(a) $CaCO_3$	
15	Hydrolysis of PI <sub>3</sub> yields:	ч	l	(c) $Ca(OH)_2$	
13.	(a) monobasic acid and a salt			[Hint: $Ca(OH)_2 + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + 2H_2O$	
	(b) monobasic acid and dibasic acid			$Ca(OH)_2 + Na_2CO_3 \longrightarrow 2NaOH + CaCO_3$	
	(c) dibasic acid and tribasic acid			$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$	
	(d) monobasic acid and tribasic acid		27	Cloudy	
	[ <b>Hint:</b> $PI_3 + 3H_2O \longrightarrow 3HI$ (monobasic) + $H_3PO_3$ (dibasic)		27.	2 7	
16.	Marshall acid is:	~/]	l	(green) (pink) (a) $(COOH)_2$ $\square$ (b) $O_3$	
10.	(a) $H_2S_2O_3$			(c) $H_2O_2$ $\square$ (d) $H_2O$	
	(c) $H_2S_2O_8$				_
17.	The geometry of $H_2S$ and its dipole moment are:		28.	$X + C + C_2 \xrightarrow{\text{High temp. of}} Y + CO$	
-/-	(a) angular and non-zero □ (b) angular and zero			noone 1000x	
	(c) linear and zero $\square$ (d) linear and non-zero			$Y + 2H_2O \longrightarrow Z + 2HCl$	
18.	HBr and HI reduce sulphuric acid HCl can reduce KMr	nO <sub>4</sub>	l	compound Y is found in polymeric chain structure and i	s an
10.	and HF reduces:			electron deficient molecule. Y is:	
	(a) $H_2SO_4$		l	(a) BeO	
	(c) KMnO <sub>4</sub> $\square$ (d) none			(c) $Be(OH)_2$ $\Box$ (d) $BeCl_2$	
19.	Which pair gives Cl <sub>2</sub> at room temperature?		l	[Hint: BeO+C+Cl <sub>2</sub> $\xrightarrow{1000 \text{ K}}$ BeCl <sub>2</sub> +CO	
	(a) Conc. $HCl + K_2Cr_2O_7 \square$ (b) $NaCl + conc. H_2SO_4$			(X) (Y)	
	(c) NaCl + MnO <sub>2</sub> $\square$ (d) NaCl + conc. HNO <sub>3</sub>		Ì	BeCl <sub>2</sub> is found in polymeric chains and is electron defic	eient.
20.				$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$	
	disintegration of:		200	(Z)	
	(a) $^{238}_{92}U$		29.	$ \begin{array}{ccc} A & +5\text{CO} \longrightarrow & I_2 & +5\text{CO}_2 \\ \text{(Colourless)} & & \text{Violet} \end{array} $	
	$(c) \frac{232}{90}$ Th $\Box (d) \frac{227}{89}$ Ac			The compound A is:	
21	In the process of extraction of gold,			(a) $I_2O_5$ $\Box$ (b) HI	
<b>4</b> 1,				(c) $HIO_3$ $\Box$ (d) $HIO_4$	
	Roasted gold ore + $CN^- + H_2O \xrightarrow{O_2} [X] + OH^-$		30.	An element used in high temperature thermometry is:	
	$[X] + Zn \longrightarrow [Y] + Au$			(a) Hg	
	Identify [X] and [Y]:			(c) Ti	
	(a) $X = [Au(CN)_2]_{\circ}^{\circ}$ ; $Y = [Zn(CN)_4]_{\circ}^{2}$		31.		ched
	(b) $X = [Au(CN)_4]^{3-}$ ; $Y = [Zn(CN)_4]^{2-}$			with hybridization of their central metal ion?	
	(c) $X = [Au(CN)_2]^-$ ; $Y = [Zn(CN)_6]_2^{4-}$			(i) $[Ni(CO)_4]sp^3$ (ii) $[Ni(CN)_4]^{2-}sp^3$	•
	(d) $X = [Au(CN)_4]^-$ ; $Y = [Zn(CN)_4]^{2^-}$			(iii) $[CoF_6]^{3-}d^2sp^3$ (iv) $[Fe(CN)_6]^{3-}sp^3d^2$	
22.	Spelter is:			Select the correct answer using the codes given below	:
	(a) impure Cu		1	(a) (i) and (ii)	
	(c) ZnO $\square$ (d) CuO			(c) (i), (iii) and (iv)	
23.		nber	1.	[ <b>Hint</b> : Ni(CO) <sub>4</sub> -sp <sup>3</sup> ; [Ni(CN) <sub>4</sub> ] <sup>2-</sup> -dsp <sup>2</sup> ]	
	is a characteristic of elements of:		I	$[\text{CoF}_6]^{3-}$ $-sp^3d^2$ ; $[\text{Fe}(\text{CN})_6]^{3-}$ $-d^2sp^3$ ]	

32.	Which one has the highest molar conductivity?  (a) Diamminedichloroplatinium (II) □  (b) Potassiumhexacyanoferrate(II) □	6.	_ (-,	
	(c) Hexaaquochromium(III) bromide (d) Pentacarbonyliron(0) □	7.	[Hint: Volume strength = $5.6 \times \text{Normality} = 5.6 \times 1.5 = 8.4$ ] Which one of the following pairs of molecules will ha	
33.	Which of the following is not an ore of magnesium?		permanent dipole moments for both members?	_
	(a) Carnallite		() 4 2	
	(c) Calamine		(-) 4 2	
34.	In the following, the element with the highest energy is:	8.	Development of a photographic plate involves the use of	_
	(a) $[Ne]3s^23p^1$			
25		ا ا	(c) a reducing agent	ш
35.	A transition metal ion exists in its highest oxidation state. It is expected to behave as:	'.		
	(a) a chelating agent			
	(b) a central metal in a coordination compound	10.	Nitrogen shows different oxidation states in the range:	_
	(c) a reducing agent	10.		
	(d) an oxidising agent		**	
Set .		11.	Which of the following is used as rocket fuel?	
			(a) liquid $O_2$ $\Box$ (b) liquid $N_2$	
1.	Recently discovered element 'ununhexium' (At. No. 116)		(c) liquid $NH_3$ $\square$ (d) liquid $H_2$	
	belongs to:	12.	Which of the following transition metal can have high	est
	(a) IInd group		oxidation state?	
2.	Chloride ion and potassium ion are isoelectronic. Then:	1	(a) Mn	
۷.	(a) their sizes are same		(c) Cu	
	(b) Cl <sup>-</sup> ion is bigger than K <sup>+</sup> ion	13.	Lead is soluble in:	
	(c) K <sup>+</sup> ion is bigger than Cl <sup>-</sup> ion		(a) $CH_3COOH$ $\square$ (b) $H_2SO_4$	
	(d) their sizes depend on other cations and anions	1	(c) HCl $\Box$ (d) HNO <sub>3</sub>	
3.	Molecular shapes of SF <sub>4</sub> , CF <sub>4</sub> and XeF <sub>4</sub> are:	14.	Copper sulphate is commercially made from copper scrap l	_
	(a) the same, with 2, 0 and 1 lone pairs of electrons		(a) heating with sodium sulphate	
	respectively		· , , , , , , , , , , , , , , , , , , ,	
	(b) the same, with 1, 1 and 1 lone pairs of electrons		(c) action of dilute H <sub>2</sub> SO <sub>4</sub> and air	
	respectively	15	(d) dissolving in hot conc. H <sub>2</sub> SO <sub>4</sub>	
	(c) different with 0, 1 and 2 lone pairs of electrons	13.	Which one of the following reactions occur at the anode the Castner process of extracting sodium metal?	111
	respectively		(a) $H_2 \longrightarrow 2H^+ + 2e^-$	
	(d) different with 1, 0 and 2 lone pairs of electrons		(a) $\Pi_2$ $\longrightarrow$ $\Pi_1$ $\longrightarrow$ $\Pi_2$ $\longrightarrow$	
	respectively	-	(c) $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$	
	[Hint: S in SF <sub>4</sub> is in $sp^3d$ hybridized state with one lone pair.		$\begin{array}{c} \text{(d) Na}^+ + e^- \longrightarrow \text{Na} \end{array}$	
	C in CF <sub>4</sub> is in $sp^3$ hybridized state with no lone pair while	16.	Compound X is anhydride of sulphuric acid. The number	of
	Xe in XeF <sub>4</sub> is in $sp^3d^2$ hybridized state with two lone pairs.]		sigma bonds and $\pi$ -bonds present in $X$ are respectively:	
1	Select the incorrect statement about $O_2^+$ and $N_2^+$ ions:		(a) 3,3	
٦.	(a) bond length of $N_2^+$ is greater than $N_2$		(c) $2,4$	
	(b) bond order of $O_2^+$ is greater than $O_2$		[Hint: The compound $X$ is $SO_3$ .]	
	(b) bond order of O <sub>2</sub> <sup>+</sup> is greater than O <sub>2</sub> □ (c) paramagnetism of O <sub>2</sub> <sup>+</sup> is less than O <sub>2</sub> □	17.	Ferrous ion changes to $X$ ion, on reacting with acidified $H_2$	
•	(d) N <sub>2</sub> is diamagnetic		The number of $d$ electrons present in $X$ and its magne	tic
	[Hint: $O_2^+$ = No. of electrons 15-Bond order 2.5, $O_2$ = Bond order		moment (in B.M.) are respectively:	_
	2; Bond order $N_2 = 3$ , Bond order $N_2^+ = 2.5$ , $O_2^+$ -one orbital		(a) 6 and 6.95	
	singly occupied, O <sub>2</sub> -two orbitals singly occupied, N <sub>2</sub> <sup>+</sup> -one	10	(c) 5 and 4.9	
	orbital singly occupied.]	10.	In acidic medium, dichromate ion oxidises ferrous ion to f	
5.	Refractory materials are used for the construction of furnaces		ric ion. If the gram molecular mass of potassium dichrom is 294 grams, its gram equivalent mass is:	alt
	because they:		(a) 294	
	(a) are light in weight		(a) 254	
	(b) can stand with high temperatures	19.	* *	
	(c) are leak proof  (d) provide oxygen to fuel  □		$B_2H_6 + 2KOH + 2X \longrightarrow 2Y + 6H_2$	
	(d) provide oxygen to fuel $\Box$	I	X and Y are respectively:	

	(a) $H_2, H_3BO_3$ $\square$ (b) $HCl, KBO_3$ $\square$	29.	What would happen when a solution of potassium chrom	nate
20	(c) $H_2O, KBO_3$ $\square$ (d) $H_2O, KBO_2$ $\square$		is treated with excess of dilute nitric acid?	_
20.	For the preparation of sodium thiosulphate by 'spring's reaction', the reactants used are:		(a) $Cr^{3+}$ and $Cr_2O_7^{2-}$ are formed	
			(b) $Cr_2O_7^{2-}$ and $H_2O$ are formed	
	( ) 2 · · · · · · · · · · · · · · · · · ·		(c) Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> is reduced to +3 state of Cr	
21	(-) 2 3 - 2		(d) $Cr_2O_7^-$ is oxidised to +7 state of $Cr$	
21.	When bauxite powder is mixed with coke and reacted with nitrogen at 2075 K, carbon monoxide and X are formed. What		[Hint: $2K_2CrO_4 + 2H^+ \longrightarrow K_2Cr_2O_7 + H_2O + 2K^+$ ]	
	is the gas formed when X is reacted with steam?	30.	In the long form of periodic table, all the non-metals and n	net-
	(a) $NH_3$ $\Box$ (b) $N_2$ $\Box$		alloids are placed with:	
	(c) $N_2O$ $\square$ (d) $O_2$ $\square$		(a) s-block $\square$ (b) d-block	Ċ
22.	Oxalic acid reacts with conc. $H_2SO_4$ to give a mixture of two		(c) $p$ -block $\square$ (d) $f$ -block	
	gases. When this mixture is passed through caustic potash	31.	<b>,</b>	
	solution, one of the gases is absorbed. The product formed is:		(a) Fused NaCl	
	(a) $K_2SO_4$ $\square$ (b) $KHCO_3$ $\square$		(c) Brine solution $\Box$ (d) Copper	
	(c) $K_2CO_3$ $\square$ (d) $KO_2$ $\square$	32.	A metal $M$ forms chlorides in its +2 and +4 oxidation sta	
	[Hint: Oxalic acid with conc. H <sub>2</sub> SO <sub>4</sub> gives CO and CO <sub>2</sub> gases.]		Which of the following statements about these chloride	
23.	The number of unpaired electrons presents in the first excited		correct? [A.I.E.E.E. 20	)06]
	state of chlorine atom is:		(a) $MCl_2$ is more volatile than $MCl_4$	
	(a) 1		(b) MCl <sub>2</sub> is more soluble in anhydrous ethanol than MCl <sub>4</sub>	
	(c) 5		(c) MCl <sub>2</sub> is more ionic than MCl <sub>4</sub>	
24.	The first important theory of coordination compounds was		(d) MCl <sub>2</sub> is more easily hydrolysed than MCl <sub>4</sub>	
	put forward by:	33.	Which of the following statements is true?[A.I.E.E. 20	006]
	(a) Slater		(a) H <sub>3</sub> PO <sub>3</sub> is stronger acid than H <sub>2</sub> SO <sub>3</sub>	
	(c) Pauling $\Box$ (d) Werner $\Box$		(b) In aqueous solution HF is a stronger acid than HCl	. 🛚
25.	Which of the following octahedral complex does not show		(c) HClO <sub>4</sub> is weaker acid than HClO <sub>3</sub>	
	geometric isomerism?		(d) HNO <sub>3</sub> is stronger acid than HNO <sub>2</sub>	
	(a) $[MA_3B_3]$ $\Box$ (b) $[MA_4B_2]$ $\Box$	34.	Nickel $(Z = 28)$ combines with a uninegative monoder	
	(c) $[MA_5B]$ $\Box$ (d) $[MA_2B_4]$ $\Box$	İ	ligand $X^-$ to form a paramagnetic complex $[NiX_4]^{2-}$ .	
26.			number of unpaired electron(s) in the nickel and geom	_
	insoluble hydroxide, $M(OH)_2$ . Its oxide $MO$ is amphoteric,		of this complex ion are, respectively: [A.I.E.E.2.2	006]
	hard and having high melting point. The alkaline earth metal	1	(a) one, tetrahedral	
	is:		(c) one, square planar $\Box$ (d) two, square planar	
	(a) Mg $\square$ (b) Ca $\square$	35.	The increasing order of the first ionisation enthalpies of	
	(c) Be		elements B, P, S and F (lowest first) is: [A.I.E.E.E. 2	006]
	[Hint: Be forms soluble BeSO <sub>4</sub> and insoluble Be(OH) <sub>2</sub> . Its oxide		(a) $F < S < P < B$ $\square$ (b) $P < S < B < F$	Ц
	BeO is amphoteric, hard and possesses high melting point.]	25	(c) $B < P < S < F$	
27.	1 0 1	36.	Match the following:	
	with same halogen $X_2$ to give $KX_3$ , a violet coloured solu-		List-II List-II	
	tion, in which halogen exists as $X_3^-$ ion, $X_2$ as a Lewis acid		1. Smelting (p) Copper glance	
	and $X^-$ as a Lewis base, halogen $X$ is:		2. Self reduction (q) Malachite	
	(a) chlorine $\Box$ (b) fluorine $\Box$	İ	3. Electrolytic reduction (r) Haematite	
	(c) bromine $\Box$ (d) iodine $\Box$		4. Hydrometallurgy (s) Bauxite	_
	$[\mathbf{Hint}: \mathbf{KI} + \mathbf{I}_2 \longrightarrow \mathbf{KI}_3 \rightleftharpoons \mathbf{K}^+ + \mathbf{I}_3^- (\mathbf{I}_2 \longleftarrow \Gamma)]$		(a) (1-r), (2-p), (3-s), (4-q)	
26	Lewis acid Lewis base  Match List I with List II and then select the correct code:		(b) (1-q), (2-p), (3-r), (4-s)	<u></u>
28.	List I List II List II		(c) (1-r), (2-s), (3-q), (4-p)	
	A. Bauxite 1. Mc-Arthur forest process		(d) $(1-r)$ , $(2-s)$ , $(3-p)$ , $(4-q)$ [ <b>Hint</b> : Smelting: Fe <sub>2</sub> O <sub>3</sub> + 3CO $\longrightarrow$ 2Fe + 3CO <sub>2</sub> ;	
	B. Argentiferrous lead 2. Froth flotation			
	C. Argentite 3. Pattinson process		Self reduction: $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$	
	D. Copper pyrites 4. Hall's method		$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$	
	A B C D		Electrolytic reduction : $Al_2O_3 + F^- \longrightarrow AlF_3$	
	(a) 4 3 1 2		$AlF_3 \Longrightarrow Al_{\downarrow}^{3+} + 3F_{\downarrow}^{-}$	
	(b) 1 2 3 4		Cathode Anode Hydrometallurgy Malachite	
	(c) 3 1 2 4		$CuCO_3 \longrightarrow CuSO_4 ]$	
	(d) 2 1 3 4		↓Fe	
	\		Cu	

37.	Halides of alkaline earth metals form hydrates		8.	Which of the following does not have optical isomer?	_
	MgCl <sub>2</sub> ·6H <sub>2</sub> O, CaCl <sub>2</sub> ·6H <sub>2</sub> O, BaCl <sub>2</sub> ·2H <sub>2</sub> O and SrCl <sub>2</sub> ·2H	I <sub>2</sub> O. This		(a) $[Co(en)_3]Cl_3$	
	shows that halides of group 2 elements:	_		(c) $[Co(en)_2Cl_2]Cl$ $\Box$ (d) $[Co(en)(NH_3)_2Cl_2]Cl$	
	(a) are hygroscopic in nature	<u> </u>	9.	Which of the following halides is least stable and doub	tful
	(b) act as dehydrating agents	91		existence?	
	(c) can absorb moisture from air	<u> </u>		(a) $PbI_4$ $\square$ (b) $SnI_4$	
	(d) all of the above			(c) $GeI_4$ $\Box$ (d) $SiI_4$	
38.	Which of the following cannot be reduced by H <sub>2</sub> O		10.	Among Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , P <sub>2</sub> O <sub>3</sub> and SO <sub>2</sub> , the correct order of a	acid
	(a) $Ag_2O$ $\Box$ (b) $Fe^{3+}$	. 🛮 📗		strength is:	
	(c) Acidified KMnO <sub>4</sub> $\square$ (d) Acidified K <sub>2</sub> Cr <sub>2</sub> O			(a) $Al_2O_3 < SiO_2 < SO_2 < P_2O_3$	
39.	Number of electrons transferred in each case when			(b) $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$	
	acts as an oxidising agent to give MnO <sub>2</sub> , Mn <sup>2+</sup> , N	$In(OH)_3$		(c) $SO_2 < P_2O_5 < SiO_2 < Al_2O_3$	
	and MnO <sub>4</sub> <sup>2</sup> , are respectively:			(d) $SiO_2 < SO_2 < Al_2O_3 < P_2O_3$	
	(a) $3, 5, 4$ and $1$		11.	The correct order of bond angles (smallest first) in H <sub>2</sub> S, N	$\Pi_3$ ,
	(c) $1, 3, 4$ and $5$			BF <sub>3</sub> and SiH <sub>4</sub> is:	
40.	$K_4Fe(CN)_6$ is used for the identification of:	· _		(a) $H_2S < SiH_4 < NH_3 < BF_3$	
	(a) $Fe^{2+}$ , $Fe^{3+}$ and $Cu^{2+}$ cations			(b) $NH_3 < H_2S < SiH_4 < BF_3$	
	(b) $Fe^{3+}$ , $Cu^{2+}$ and $Zn^{2+}$ cations			(c) $H_2S < NH_3 < SiH_4 < BF_3$	
	(c) $Fe^{2+}$ , $Fe^{3+}$ and $Zn^{2+}$ cations			(d) $H_2S < NH_3 < BF_3 < SiH_4$	
	(d) Fe <sup>2+</sup> , Fe <sup>3+</sup> and Ni <sup>2+</sup> cations		12.	Which one of the following has the regular tetrahe	dral
	[Hint: $Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3$		•	structure?	
	Prussian blue $Cu^{2+} + [Fe(CN)_6]^{4-} \longrightarrow Cu_2[Fe(CN)_6]$			(a) $XeF_4$ $\Box$ (b) $SF_4$	
	$\operatorname{Cu}^- + [\operatorname{Fe}(\operatorname{CN})_6]  \operatorname{Cu}_2[\operatorname{Fe}(\operatorname{CN})_6]$ Chocolate			(c) $BF_4^-$	
		Į	13.	Of the following outer electronic configurations of atoms,	
	$\operatorname{Zn}^{2+} + [\operatorname{Fe}(\operatorname{CN})_6]^{4-} \longrightarrow \operatorname{Zn}_2[\operatorname{Fe}(\operatorname{CN})_6]$ Bluish white	1		highest oxidation state is achieved by which one of the	_
Set		•		(a) $(n-1)d^8ns^2$	
1.	The bond lengths in the species $O_2$ , $O_2^+$ and $O_2^-$ a	re in the		(c) $(n-1)d^3ns^2$	
	order:		14.	Beryllium and aluminium exhibit many properties which	are
•	(a) $O_2^+ > O_2^- > O_2$	- 🗆		similar. But the two elements differ in:	_
	(c) $O_2 > O_2^{+} > O_2^{-}$			(a) exhibiting maximum covalency in compounds	ᆸ
	[Hint: Bond order $O_2^- = 1.5$ , $O_2 = 2.0$ and $O_2^+ = 2.5$ ]			(b) forming polymeric hydrides	
2.	S—S bond is not present in:			(c) forming covalent halides	
	(a) $H_2S_2O_4$		4.00	(d) exhibiting amphoteric nature in their oxides	. ⊔
	(c) $H_2S_2O_8$ $\square$ (d) none of these		15.	Which process of purification is represented by the foll	.ow-
3.	The normality of a mixture obtained by mixing 100 r	nL of 0.2		ing scheme?	
	$M  \text{H}_2 \text{SO}_4 + 100  \text{mL of } 0.2  M  \text{NaOH is}$ :			$\begin{array}{ccc} \text{Ti} & + & 2I_2 & \xrightarrow{250^{\circ}\text{C}} & \text{Ti}I_4 & \xrightarrow{1400^{\circ}\text{C}} & \text{Ti} & + & 2I_2 \\ \text{Impure} & & & & & & & & & & & \\ \end{array}$	
•	(a) $0.2$			(a) Cupellation $\square$ (b) Poling	
	(c) $0.1$ $\Box$ (d) $0.3$			(c) Zone refining	
	[Hint: $0.2 M H_2SO_4 = 0.4 N H_2SO_4$ ]		16.	Which of the hydrogen halides form salts like K	
4.	How many unpaired electrons are there in Ni <sup>2+</sup> ior			(where X is a halogen atom):	
	(a) 2	<u> </u>		(a) HF	
_	(c) 8			(c) HBr	
5.	,	ores, the	17.	In the electrothermal process, the compound displaced	
	particles of the ore float because:			silica from calcium phosphate is:	- 0,
	(a) they are light $\Box$ (b) they are insolub			(a) calcium phosphide $\square$ (b) phosphine	
	(c) they bear electrostatic charge			(c) phosphorus pentoxide	
	(d) their surface is not easily wetted by water			(d) phosphorus	
6.	Among the halogens, the one which is oxidised by n	utric acid	18.	An important product in the ozone depletion by chlorofly	
	is:			carbons is:	
	(a) F		* .	(a) Cl <sub>2</sub>	
,,	(c) Br			(c) $OF_2$ $\square$ (d) $O_2F_2$	
7.		organo-	19.	The element with atomic number 118, if discovered, wi	
	metallic compound?			placed in:	,
	(a) Ferrocene			(a) Ist group	
	(c) Zeise's salt	t 🗆	l	(c) 16th group  (d) 18th group	П

20.	On the basis of electronic configuration, the known element	ents	30.	• •	oxidation state of a metal in	aque-
	are grouped in:			ous solution is determine	<del>-</del>	
	(a) 3-blocks $\square$ (b) 2-blocks			(a) enthalpy of sublimation	on of the metal	
	(c) 4-blocks + lanthanides			(b) ionisation energy		
	(d) 3-blocks + lanthanides + actinides			(c) enthalpy of hydration	of the metal ion	
21.	When hydrolith is treated with water, it yields:			(d) all of the above		
	(a) $H_2$		31.	Which of the following i	is the most basic oxide?	
	(c) $NH_3$			(a) $Bi_2O_3$	□ (b) SeO <sub>2</sub>	
22.	1000 g aqueous solution of CaCO <sub>3</sub> contains 0.1 g of CaC	O <sub>3</sub> .		(c) $Al_2O_3$	$\Box$ (d) Sb <sub>2</sub> O <sub>3</sub>	
	Hardness of this solution is:		32.	Which of the following s	species has a linear shape?	
	(a) 1000 ppm			(a) $NO_2^+$	$\square$ (b) $NO_2^-$	
	(c) 10 ppm			(c) O <sub>3</sub>	$\square$ (d) $SO_2$	
23.	A compound which can be used in space vehicles both	n to	33.		set is not in accordance wit	th the
	absorb CO <sub>2</sub> and liberate oxygen is:			property stated against i		
	(a) NaOH			(a) $F_2 > Cl_2 > Br_2 > I_2$ :		
	(c) Na <sub>2</sub> O <sub>2</sub>				bond dissociation energy	
24.	The highest ionisation potential in a period is shown by			(c) $F_2 > Cl_2 > Br_2 > I_2 : c$		
	(a) noble gases	, 			F: acidic property in water	
	(c) alkaline earth metals  (d) halogens		34.		and select the correct answer	
25.	Which form contains the maximum percentage of carbo		1 "	the codes given below the		asmi
<b></b>	(a) Wrought iron $\square$ (b) Steel			_		
	(c) Cast iron			List-I	List-II	
26.			İ	<ol> <li>Oxide ore</li> </ol>	A. Feldspar	
20.	number of outer shell electrons of X. The X may belong			2. Sulphide ore	B. Barytes	
	(a) p-block of periodic table	, to.		3. Sulphate ore	C. Fluorspar	
	(b) group 8 of periodic table			4. Halide ore	D. Galena	
					E. Corundum	
	(c) d-block of periodic table		ĺ		□ (b) 1-B, 2-D, 3-C, 4-A	
27	(d) s-block of periodic table			(c) 1–B, 2–D, 3–E, 4–A	☐ (d) 1–E, 2–D, 3–B, 4–C	
27.	The hair dye available in the market generally contains		35.	Match List-I and List-II a	and pick out correct matching	codes
	bottles one containing dye and other containing hydro	_	1	from the given choices:		
	peroxide. The bottles are mixed before applying. The fund	uon	Į	List-I	List-II	
	of hydrogen peroxide is:			A. CIF <sub>3</sub>	Square planar	
	(a) to dilute the dye		]	B. PCl <sub>5</sub>	Tetrahedral	
	(b) to oxidise the dye to give desired colour		İ	C. IF <sub>5</sub>	Trigonal bipyramidal	
	(c) to reduce the dye to give desired colour		}	D. CCl <sub>4</sub>		
	(d) to acidify the dye			E XeF <sub>4</sub>	4. Square pyramidal	
28.	$B \xrightarrow{Z} X \xrightarrow{\text{LiH}} Y + \text{LiBF}_4$			·	5. T-shaped	
	↑ Heat			(a) A-5, B-4, C-3, D-2,		_
	Which of the following statements is true for the at	ove		(b) A-5, B-3, C-4, D-2,		
	sequence of reactions?			(c) A-5, B-3, C-4, D-1,		
	(a) Z is hydrogen $\Box$ (b) $X$ is $B_2H_6$		26	(d) A-4, B-3, C-5, D-2,		. 🗖
	(c) X is fluorine and Y is B <sub>2</sub> H <sub>6</sub>		30.	All oxides of which of the	_	
	(d) Z is potassium hydroxide			1. Al (III) 2. Pb (II) 3.		
	[Hint: $B + F_2 \longrightarrow BF_3 \xrightarrow{LiH} B_2H_6 + LiBF_4$ (Z) (X) (Y) Heat (Z) Heat			(a) 1 and 3 only	$\square$ (b) 1, 2 and 3	
	$(Z) \qquad (X) \qquad (Y) \qquad (Y) \qquad (Z)$			(c) 3 and 4 only	☐ (d) None of these	
	$(Z) \qquad (X) \qquad (Y) \qquad \underset{\text{Heat}}{\overset{(Y)}{\longmapsto}} B + H_2 ]$		37.	The correct order of ma	tching of the following comp	ounds
20	In N <sub>2</sub> O, the N—N distance pertains to:			is:		
<i>. ورسد</i>	(a) N=N bond			List-I	List-II	
	(b) N=N bond		1	A. Borazole		
	(c) N—N bond			B. Plaster of Paris	1. CaSO <sub>4</sub> ·1/2 H <sub>2</sub> O	
	(d) intermediate of N=N and N≡N			C. Boric acid	2. C <sub>60</sub>	
		<u></u>			3. SiO <sub>2</sub>	
	[Hint: N <sub>2</sub> O is a resonance hybrid of following structures		1	D. Quartz	4. $B_3N_3H_6$	
	$\ddot{\mathbf{N}} = \dot{\mathbf{N}} = \dot{0} \longleftrightarrow \mathbf{N} = \dot{\mathbf{N}} - \dot{0} : \bar{0}$			E Buckminsterfullerene	e 5. H <sub>3</sub> BO <sub>3</sub> [ <b>P.M.T.(Kerala</b> )	20101
	•		1		T.W. L. INCIAIA)	401U

	(a) A-3, B-1, C-2, D-5, E-4 (b) A-1, B-5, C-3, D-4, E-2		9.	Which of the following is used as a moderator in nuclear reactors?	
	(c) A-5, B-2, C-1, D-3, E-4			·	
				(a) Heavy hydrogen	
	(d) A-4, B-1, C-5, D-3, E-2	¦	10	(c) Heavy water	
20	(e) A-4, B-1, C-5, D-2, E-3	_	. 10.	Which of the following has largest solubility in water?	
38.	Among the oxides,			(a) $Ba(OH)_2$ $\Box$ (b) $Sr(OH)_2$ $\Box$	
	1. $Mn_2O_7$ 2. $V_2O_3$ 3. $V_2O_5$ 4. CrO 5. $Cr_2O_3$			(c) $Ca(OH)_2$ $\Box$ (d) $Mg(OH)_2$ $\Box$	
	the basic oxides are : [P.M.T. (Kerala) 20 $\Box$ (b) 2 and 3	10]	11.	Which of the following is not an important constituent of cement?	•
		_			
	(c) 3 and 4			(a) CaO $\square$ (b) Al <sub>2</sub> O <sub>3</sub> $\square$	
39.				(c) MgO $\square$ (d) Na <sub>2</sub> O $\square$	•
	[Fe(H <sub>2</sub> O) <sub>5</sub> NO] <sup>2+</sup> which is formed during the 'ring test' is	s:	12.	The electronic configuration of an element is $1s^2, 2s^2 2p^6$ ,	,
	(a) 2			$3s^23p^63d^5$ , $4s^1$ . This represents its:	
	(c) 4			(a) excited state $\Box$ (b) ground state $\Box$	
40.	$Hypo + I_2 \longrightarrow A$			(c) cationic form $\Box$ (d) anionic form $\Box$	Į
	$Hypo + Cl_2 \longrightarrow B$		13.	Which of the following halides is most acidic?	
	A and B are :			(a) $BCl_3$ $\Box$ (b) $SbCl_3$ $\Box$	l
		_		(c) BiCl <sub>3</sub> $\square$ (d) CCl <sub>4</sub> $\square$	
	(a) $A = \text{Na}_2\text{S}_4\text{O}_6$ and $B = \text{Na}_2\text{SO}_4$		14.	Which acid forms two series of salts?	
	(b) $A = \text{Na}_2\text{S}_4\text{O}_6$ and $B = \text{NaHSO}_4$			(a) $H_3PO_4$ $\square$ (b) $H_3PO_3$ $\square$	ĺ
	(c) Both A and B are $Na_2S_4O_6$			(c) $H_3BO_3$ $\square$ (d) $H_3PO_2$ $\square$	ĺ
	(d) Both A and B are Na <sub>2</sub> SO <sub>4</sub>		15.	The number of P—O—P bonds in cyclic meta-phosphoric	
	[Hint: $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$ ;		10.	acid is:	
	$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl]$			(a) one $\Box$ (b) two $\Box$	ı
•			1	(c) three $\Box$ (d) four $\Box$	
Set	<b>5</b>		16	_ (-,	,
1.	Consider the cations, Li <sup>+</sup> , Be <sup>2+</sup> , Mg <sup>2+</sup> , K <sup>+</sup> and Al <sup>3+</sup> .	The	10.	The type of hybridization of boron in diborane is:  (a) $c^{2}$	1
	largest and the smallest ions from this list are respectiv			(a) $sp$ $\Box$ (b) $sp^2$ $\Box$ (c) $dsp^3$	_
	(a) $K^+$ and $Li^+$ $\Box$ (b) $Al^{3+}$ and $Be^{2+}$		٠		_
	(c) $Mg^{2+}$ and $Li^{+}$ $\square$ (d) $K^{+}$ and $Be^{2+}$		17.	Ammonium dichromate is used in some fire works. The green coloured powder blown in air is:	ł
2.	The outermost electronic configuration of the most electronic	etro-		(a) CrO <sub>3</sub>	1
	negative element (from the list below) is:			(c) Cr $\square$ (d) CrO(O <sub>2</sub> ) <sub>2</sub> $\square$	
	(a) $3s^23p^3$		18.		
	(c) $3s^23p^1$		10.	(a) Zr and Hf have about the same radius	_
				(b) Zr and Nb have similar oxidation states	
3.	The cation containing maximum number of unpaired elect	rons		(c) Zr and Y have about the same radius	
	is:			* *	
	(a) $Co_{2}^{2+}$		10		
	(c) $Fe^{3+}$		19.	Number of moles of $K_2Cr_2O_7$ reduced by 1 mole of $Sn^{2+}$ is	-
4.	The atomic property which is not periodic is:			(a) 1/6	
	(a) atomic radius			(c) 1/3	
	(c) electronegativity		l	[Hint: $(\operatorname{Sn}^{2+} \longrightarrow \operatorname{Sn}^{4+} + 2e^{-}) \times 3$ , $(\operatorname{Cr}_{2}\operatorname{O}_{7}^{2-} + 6e^{-} \longrightarrow 2\operatorname{Cr}^{3+})$	
5.	The carbide that gives methane on hydrolysis is:		1	<i>i.e.</i> , 3 moles of $\operatorname{Sn}^{2+}$ react with one mole of $\operatorname{Cr}_2\operatorname{O}_7^{2-}$ . Thus	,
	(a) $Al_4C_3$			one mole of $Sn^{2+}$ reacts with 1/3 mole of $K_2Cr_2O_7$ .]	
	(c) $CaC_2$ $\Box$ (d) $TiC$		20.	Which transition metal has the highest density?	
6.	In solid CuSO <sub>4</sub> ·5H <sub>2</sub> O, copper is coordinated to:	(		(a) $Zn$ $\Box$ (b) $Sc$	]
	(a) one water molecule $\Box$ (b) one sulphate ion			(c) La	1
	(c) four water molecules  (d) five water molecules		21.		
7.				(a) Sc	1
	periodic table is:	r		(c) Tc $\Box$ (d) Zr	
	(a) ionisation energy		22.	• • •	•
	(c) electron affinity		22.	(a) potassium aluminium oxalate	7
0	- · · · · · · · · · · · · · · · · · · ·	لسا	I	(b) potassium aluminium (III) trioxalate	
8.	Which hybrid state cannot be shown by carbon?	_		(c) potassium trioxalatoaluminate (III)	
	(a) $sp^3d$				
	(c) $sp^2$		1	(d) potassium tris (oxalato) aluminium	L

23.	Which one of the following ligands forms a chelate?	1	(a) $[Fe(CN)_6]^{4-}$
	(a) Acetate	1	(c) $[Pt(CN)_4]^{2-}$
	(c) Cyanide	36.	1, 2 1, 2, 3
24.	Among the following ions which one has the highest	1	well as reducing agent? [P.E.T. (Kerala) 2010]
	paramagnetism?		(a) $C\Gamma$ $\Box$ (b) $ClO_4^ \Box$
	(a) $[Fe(H_2O)_6]^{3+}$		(c) $ClO^ \Box$ (d) $MnO_4^ \Box$
	(a) $[Fe(H_2O)_6]^{3+}$	Ì	• • • • • • • • • • • • • • • • • • • •
25.	The major air pollutant is:	1	(e) $NO_3$
	(a) oxides of nitrogen $\Box$ (b) oxides of sulphur $\Box$		[Hint: In all the given species except ClO, the central elements
	(c) soot $\square$ (d) carbon monoxide $\square$	1	are either in their maximum or minimum oxidation state
26.	Coordination number of $Cu^{2+}$ is in $CuSO_4.5H_2O$ :		and hence, they cannot further increase or decrease the oxidation states. In ClO, the oxidation state of Cl can be
	(a) 5		increased or decreased i.e., it can act as oxidising as well
	(c) 3 $\square$ (d) 2 $\square$		as a reducing agent.]
27.	Which of these molecules have nonbonding electron pairs	37.	The correct increasing order of paramagnetism of
•	on the central atom?	1	(i) MnSO <sub>4</sub> ·4H <sub>2</sub> O (ii) FeSO <sub>4</sub> ·7H <sub>2</sub> O (iii) NiSO <sub>4</sub> ·6H <sub>2</sub> O
	I SF <sub>4</sub> II ICl <sub>3</sub> III SO <sub>3</sub>		·
	(a) II only $\square$ (b) I and II only $\square$		(iv) CuSO <sub>4</sub> ·5H <sub>2</sub> O is:
	(c) I and III only	1	(a) (i) $<$ (ii) $<$ (iii) $<$ (iv) $\square$ (b) (iv) $<$ (iii) $<$ (i) $\square$
28.	The ionisation potential of nitrogen is:		(c) $(iii) < (iv) < (ii) < (i)$
	(a) same as that of oxygen		[Hint: Mn <sup>2+</sup> (5 unpaired electrons), Fe <sup>2+</sup> (4 unpaired electrons),
	(b) less than that of oxygen		Ni <sup>2+</sup> (2 unpaired electrons) and Cu <sup>2+</sup> (one unpaired
	(c) greater than that of oxygen		electron).]
20	(d) none of the above	38.	<u> </u>
29.	2		from the codes given below:
	be:		List-I List-II
	(a) $Be_2C$ $\square$ (b) $CaC_2$ $\square$		A. [Ag(CN) <sub>2</sub> ] 1. Square planar and 1.73 B.M.
20	(c) SiC $\square$ (d) Mg <sub>2</sub> C <sub>3</sub> $\square$	-	
30.	2	1	B. $[Cu(CN)_4]^{3-}$ 2. Linear and Zero
	(a) $HClO_3$ to $HCl$ $\Box$ (b) $Cr_2O_7^{2-} + H^+$ to $Cr^{3+}$ $\Box$ (c) $MnO_4^- + H^+$ to $Mn^{2+}$ $\Box$ (d) all of these $\Box$		C. $[Cu(CN)_6]^4$ 3. Octahedral and Zero
21	The sequence that correctly describes the relative bond	1	D. $[Cu(NH_3)_4]^{2+}$ 4. Tetrahedral and Zero
31.	strength pertaining to oxygen molecule and its cation or	İ	E. $[Fe(CN)_6]^{4-}$ 5. Octahedral and 1.73 B.M.
	anion is:		(a) A-2, B-4, C-5, D-1, E-3
	(a) $O_2^{-} > O_2^{-} > O_2 > O_2^{+}$ $\square$ (b) $O_2 > O_2^{+} > O_2^{-} > O_2^{2-}$ $\square$		(b) A–5, B–4, C–1, D–3, E–2 □
			(c) $A-1$ , $B-3$ , $C-4$ , $D-2$ , $E-5$
	(c) $O_2^+ > O_2 > O_2^{2-} > O_2^ \Box$ (d) $O_2^+ > O_2 > O_2^- > O_2^{2-}$ $\Box$		(d) A-4, B-5, C-2, D-1, E-3
	[Hint: Bond order $O_2^+ = 2.5$ , $O_2 = 2$ , $O_2^- = 1.5$ and $O_2^{2-} = 1.0$	39.	
	Relative bond strength ∞ bond order]	1	given below:
32.	The 'Bordeaux mixture' is:		$4Au + 8NaCN + H_2O + X \longrightarrow 4Na[Au(CN)_2] + 4NaOH$
	(a) copper sulphate and borax		$\downarrow_Y$
	(b) orthoboric acid and ferrous sulphate		Au
	(c) sodium borate and zinc sulphate		X and Y in the reaction are:
22	(-) France	1	(a) $N_2$ and $Cu$ $\square$ (b) $O_2$ and $Zn$ $\square$
33.	Among the following complexes, which has a magnetic moment of 5.9 BM?	1	(c) $CO_2$ and $Ni$ $\Box$ (d) $CO_2$ and $Ag$ $\Box$
	Ni(CO) <sub>4</sub> , $[Fe(H_2O)_6]^{2+}$ , $[Co(NH_3)_6]^{3+}$ , $[MnBr_4]^{2-}$	40.	A metal $M$ readily forms $MSO_4$ which is water soluble. It
	(a) Ni(CO) <sub>4</sub> $\Box$ (b) $[Fe(H_2O)_6]^{2+}$ $\Box$		forms an insoluble hydroxide $M(OH)_2$ which is soluble in
	(a) Ni(CO) <sub>4</sub>	ľ	excess of NaOH solution. The metal $M$ is:
34.	Which of the following statements is not correct about	l	(a) Mg
·	diborane?		(b) Ba
	(a) The B atoms are in $sp^3$ hybrid state $\Box$		(c) Be
	(b) It contains two 3 centre-2 electron bonds	1	(d) cannot be determined as data is incomplete
	(c) The B-H bond lengths in it are equal due to resonance		•
		Set	t <b>6</b>
	(d) The molecule is non-planar	1.	Hydrogen gas will not reduce:
35.			(a) heated cupric oxide $\Box$ (b) heated ferric oxide $\Box$
		1	(c) heated stannic oxide \( \square\) (d) heated aluminium oxide \( \square\)

2.	A solution of sodium sulphate in water is electrolysed us	ing	17.	The hybridization of I in $I_3^-$ ion is:
	inert electrodes. The products at the cathode and anode		1	(a) $sp^3$ $\square$ (b) $sp^3d$ $\square$
	respectively:		l	(c) $sp^3d^2$
	(a) $H_2, O_2$		18.	* * *
	(c) $O_2$ , $Na$ $\square$ (d) $O_2$ , $SO_2$		10.	(a) NH <sub>3</sub>
3.	Which oxide of nitrogen is a coloured gas?	_	[	(*)
	(a) $N_2O$ $\square$ (b) $NO$		10	· · · · · · · · · · · · · · · · · · ·
	(c) $NO_2$ $\square$ (d) $N_2O_5$		15.	In which case the energy released is minimum in the process?
4.	Ammonia with excess of Cl <sub>2</sub> gives mainly:		}	(a) $N \longrightarrow N^-$
	(a) $N_2$ and $NH_4Cl$ $\square$ (b) $NCl_3$ and $HCl$		20	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
	(c) $NCl_3$ and $NH_4Cl$ $\square$ (d) none of these		20.	The correct order of acidic strength is:
5.	Which sulphate on strong heating gives SO <sub>2</sub> and SO <sub>3</sub> ?			(a) $Na_2O > MgO > Al_2O_3 \square$ (b) $K_2O > CaO > MgO \square$
٥,	(a) FeSO <sub>4</sub>		Í	(c) $CO_2 > N_2O_5 > SO_3$ $\square$ (d) $Cl_2O_7 > SO_2 > P_4O_{10}$ $\square$
	(c) $Fe_2(SO_4)_3$ $\square$ (d) $CaSO_4$		21.	A white solid reacts with dilute HCl to give a colourless gas
6.	The type of hybrid orbitals used by the chlorine atom			that decolourises aqueous bromine. The solid is most likely:
٠.	$ClO_2$ is:	1111	l	(a) sodium carbonate
	(a) $sp^3$ $\Box$ (b) $sp^2$			(c) sodium acetate $\Box$ (d) sodium thiosulphate $\Box$
	(c) $sp$ $\square$ (d) none of these			[Hint: $Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + S + SO_2 + H_2O;$
7	Which of the following statements are correct for CsBr <sub>3</sub>			$SO_2 + Br_2 + 2H_2O \longrightarrow 2HBr + H_2SO_4$
/.	(a) It is a covalent compound		22.	Transition metals form complexes because of:
	(b) It contains Cs <sup>3+</sup> and Br <sup>-</sup> ions			(a) small cation size $\Box$ (b) vacant d-orbitals $\Box$
	(c) It contains Cs <sup>+</sup> , Br <sup>-</sup> and lattice Br <sub>2</sub> molecule			(c) large ionic charge $\Box$ (d) all of these $\Box$
	(d) It contains $Cs^+$ and $Br_3^-$ ions		23.	8 - Start of 11202 regulated to him of 14 intimora
8.	The correct order of increasing C—O bond length of (			solution in a titration in the presence of H <sub>2</sub> SO <sub>4</sub> , the purity of
٠.	$CO_3^{2-}$ and $CO_2$ is:	٠٠,		$H_2O_2$ is:
	(a) $CO_3^{2-} < CO_2 < CO$ $\Box$ (b) $CO < CO_2 < CO_3^{2-}$	_		(a) 25%
	(a) $CO_3 \times CO_2 \times CO = (b) CO \times CO_2 \times CO_3$			(c) 85%
0	(c) $CO_2 < CO_3^2 < CO \square$ (d) $CO < CO_3^2 < CO_2$		24.	1
7.	Concentrated aqueous sodium hydroxide can separate	a	l ·	(a) $ZnO$ $\square$ (b) $ZnCO_3$ $\square$
	mixture of:			(c) $ZnSO_4$ $\square$ (d) $ZnCl_2$ $\square$
	(a) $Al^{3+}$ , $Sn^{2+}$		25.	Turnbull's blue is a compound having formula:
	(c) $Al^{3+}$ , $Zn^{2+}$ $\Box$ (d) $Pb^{2+}$ , $Zn^{2+}$			(a) KFe (III) [Fe (II) (CN) <sub>6</sub> ] $\Box$
10.	On heating chromite (FeCr <sub>2</sub> O <sub>4</sub> ) with Na <sub>2</sub> CO <sub>3</sub> in air,	the	ļ	(b) KFe (II) [Fe (III) (CN) <sub>6</sub> ] $\Box$
	following product is obtained:			(c) $Na_2$ [Fe (CN) <sub>5</sub> NO]
	(a) $Na_2CrO_4$			(d) $\operatorname{Fe}_4[\operatorname{Fe}(\operatorname{CN})_6]_3$
	(c) FeO $\Box$ (d) Fe <sub>3</sub> O <sub>4</sub>		26.	Use of freons as aerosol propellant is to be discouraged
11.	Iodine is formed when potassium iodide reacts with:	1	1	because:
	(a) $ZnSO_4$ $\Box$ (b) $FeSO_4$			(a) they are toxic
	(c) $CuSO_4$			(b) they are very reactive
12.	Which halide is not oxidised by MnO <sub>2</sub> ?			(c) they are corrosive
	(a) $I^-$			(d) they destroy ozone layer
	(c) $CI^-$		27.	B
13.	Which metal burns in air at high temperature with	the		20 mL of 0.5 N caustic potash. The basicity of the acid is:
	evolution of much heat?			(a) 1
	(a) Cu		1	(c) 3
	(c) Pb		28.	Match
14.	The carbide which yields propyne on hydrolysis:			(1) CO <sub>2</sub> (A) Pyramid
	(a) $Al_4C_3$ $\Box$ (b) $Be_2C$			(2) SO <sub>2</sub> (B) Tetrahedral
	(c) $Mg_2C_3$			(3) BF <sub>3</sub> (C) Triangular planar
15.	Paramagnetism is not shown by:			(4) CH <sub>3</sub> <sup>+</sup> (D) Linear
	(a) $Cl_2O_7$ $\Box$ (b) $ClO_3$			(E) Angular
	(c) $O_2$ $\square$ (d) $ClO_2$			1 2 3 4
16.	The metal present in vitamin B <sub>12</sub> is:			(a) C E D B
	(a) Fe			(b) D E C A
	(c) Mg $\Box$ (d) Mn			(c) D E C C $\square$
				(d) D E B B

29.	Which of the following is prepared by electrolytic method?	The correct match of contents in Column-I with those in
	(I) Mg (II) $F_2$ (III) Sn (IV) S	Column-II is: [P.E.T. (Kerala) 2008]
	(a) I and II	(a)· A-iii, B-i, C-ii, D-iv
	(c) III and IV	(c) A-i, B-ii, C-iii, D-iv
30.	Hybridization in $I_3$ is:	(e) A-ii, B-iv, C-i, D-iii □
20.	(a) $sp^3$ $\Box$ (b) $sp^3d$ $\Box$	39. Match the List-I and List-II employed in the manufacture of
	(c) $sp^3d^2$ $\Box$ (d) $dsp^2$ $\Box$	substances and select the correct option:
21	Number $f$ in	-
31.	Number of unpaired electrons in $[Co(F_6)]^{3-}$ is:	[C.B.S.E. (P.M.T.) 2010]
	(a) 4	List-II List-II
	(c) 3 $\square$ (d) 1 $\square$	(Substances) (Processes)
	[Hint: $Co^{3+}$ has configuration [Ar] $3d^6$ . It undergoes $sp^3d^2$	A. Sulphuric acid (i) Haber process
	hybridization, i.e., it has four unpaired electrons.]	B. Steel (ii) Bessemer process
32.	Hydrolysis of XeF <sub>4</sub> and CaNCN gives respectively:	C. Sodium hydroxide (iii) Leblanc process
	[J.E.E. (Orissa) 2006]	D. Ammonia (iv) Contact process
	(a) $XeO_3$ and $CaCO_3$ $\square$ (b) $XeO_2$ and $CaCN_2$ $\square$	(a) A-(i), B-(iv), C-(ii), D-(iii)
	(c) $XeOF_3$ and $CaCN_2$ $\square$ (d) $XeOF_2$ and $CaCO_3$ $\square$	(b) A-(i), B-(ii), C-(iii), D-(iv)
	[Hint: $2XeF_4 + H_2O \longrightarrow XeO_3 + Xe + F_2 + 6HF$	(c) $A$ -(iv), $B$ -(iii), $C$ -(ii), $D$ -(i)
	$\begin{array}{c} \text{CaNCN} + 3\text{H}_2\text{O} \longrightarrow \text{CaCO}_3 + 2\text{NH}_3 \end{array}]$	(d) $A$ -(iv), $B$ -(ii), $C$ -(iii), $D$ -(i)
	· •	40. Which of the following exhibits square pyramidal geometry?
33.	The gases produced in heating $Pb(NO_3)_2 \xrightarrow{\Delta} \dots$ and	
	$NH_4NO_3 \xrightarrow{\Delta} \dots$ are respectively:	[A.M.U. (Engg.) 2010]
	(a) $N_2O,NO$ $\square$ (b) $N_2O,NO_2$ $\square$	(a) $XeF_6$
		(c) $BrF_5$ $\square$ (d) $XeF_4$ $\square$
	(c) NO, NO <sub>2</sub> $\Box$ (d) NO <sub>2</sub> , N <sub>2</sub> O $\Box$	Multiple Choice—B
	[Hint: $Pb(NO_3)_2 \longrightarrow PbO + 2NO_2 + \frac{1}{2}O_2$	maniple onoice b
	$NH_4NO_3 \longrightarrow N_2O + 2H_2O$	The following questions have one or more correct answer(s)
34,	The ore having two different metal atoms is:	for each of them. Choose the correct answer(s).
<i>5</i> 11	(a) haematite	Set 1
	(c) magnetite	
35	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> reacts with NH <sub>4</sub> Cl and H <sub>2</sub> SO <sub>4</sub> . The product formed	1. The long form of the periodic table has:
JJ.	is:	(a) seven horizontal rows representing seven periods
		(b) eighteen vertical columns representing eighteen groups
	(a) chromous chlorate with green vapour	(c) eight vertical columns representing $d$ -block elements $\square$
	(b) chromous chloride with white vapour	(d) six vertical columns representing $p$ -block elements $\square$
	(c) chromous chloride with blue vapour	2. Which of the following molecules do possess a permanent
	(d) chromyl chloride with deep red vapour $\Box$	dipole moment?
36.	Which one of the following is the correct statement?	(a) $H_2S$ $\square$ (b) $SO_2$ $\square$
	[A.I.E.E.E. 2008]	(c) $NH_3$ $\square$ (d) $CS_2$ $\square$
	(a) $B_2H_6 \cdot 2NH_3$ is known as inorganic benzene	3. Which of the following molecules have a linear arrangement
	(b) Boric acid is a protonic acid	of atoms?
	(c) Beryllium exhibits coordination number of six	(a) $H_2S$ $\square$ (b) $XeF_2$ $\square$
	(d) Chlorides of both Be and Al have bridged chloride	(c) $C_2H_2$ $\Box$ (d) $BeCl_2$ $\Box$
	structures in solid phase	4. Correct statements are:
37.	The incorrect statement(s) among the following is/are:	(a) Calamine and siderite are carbonates
	[P.E.T. (Kerala) 2008]	(b) Argentite and cuprite are oxides
	(i) NCl <sub>5</sub> does not exist while PCl <sub>5</sub> does	(c) Zinc blende and iron pyrites are sulphides
	(ii) Lead prefers to form tetravalent compounds	(d) Malachite and azurite are ores of copper
	(iii) The three C—O bonds are not equal in the carbonate	5. Which of the following gases on dissolution in water make
	ion	the solution acidic?
	(iv) Both O <sub>2</sub> and NO are paramagnetic	
	(a) (i), (iii) and (iv) $\Box$ (b) (i) and (iv) $\Box$	(a) CO $\Box$ (b) CO <sub>2</sub> $\Box$
	(c) (ii) and (iii) $\Box$ (d) (i) and (iii) $\Box$	(c) $SO_3$ $\square$ (d) $PH_3$ $\square$
	(e) (iv) only	6. Which of the following alloys contains Cu and Zn?
38.	Column-II Column-II	(a) Bronze
J.J.	(A) He (i) High electron affinity	(c) Gun metal $\Box$ (d) Type metal $\Box$
	(B) Cl (ii) Most electropositive element	7. The compounds used as refrigerant are:
		(a) $NH_3$ $\square$ (b) $CCl_4$ $\square$
	(C) Ca (iii) Strongest reducing agent	(a) $RH_3$ $\Box$ (b) $CC_4$ $\Box$ (c) $CF_2$ $\Box$

0	700	4. *			1 24	December of the last of the			
8.	The species that do not co		_	-	24.	Property not characterist			_
	· · -	-	b) MnO <sub>2</sub>			(a) coloured salts		(b) paramagnetic	
	(-)2		(d) Na <sub>2</sub> O <sub>2</sub>		~~	(c) fixed valency		(d) low density	
9.	The alkali metals:				25.	Transition elements with	4s^ c	onfiguration in the ground	state
	(a) form salt like hydrides					are:	_		
	(b) possess low ionisation	n pote	ential values			(a) Cr		(b) Mn	
	(c) have low density					(c) Cu		(d) Ni	
	(d) have high affinity for	non-r	netals		Set	2			
10.	Oxide minerals of aluminic	ım are	e:	,	1	Electron affinity of:			
	(a) cryolite		b) corundum		1.	(a) carbon is greater tha	n ox	voen	
	(c) bauxite		(d) diaspore			(b) sulphur is higher that			
11.	The compounds obtained			oric		(c) chlorine is higher that			
	acid are:	•				(d) chlorine is higher that			
	(a) metaphosphoric acid		b) pyrophosphoric acid		2.	While reviewing the third			
			(d) $P_4O_{10}$		2.	out the correct statemen		eichients in periodic table,	bour
12.	Which does/do not exist?		(4) 14010					70	
12.			(b) PbCl <sub>4</sub>			<ul><li>(a) sodium has the large</li><li>(b) chlorine has the max</li></ul>			
			(d) PbI <sub>4</sub>			* *			
13.	Halogens are:	<b>ш</b> (	(u) 1 014	L	1	_	uai (	of Mg > first ionisation p	
13.	_		(h) viarri manativia			tial of aluminium		1 .	닏
	` '		(b) very reactive			(d) chlorine is the stron			
	(c) electronegative		•		3.	Choose the molecules in	wh	ich hybridization occurs i	n the
1.4	(d) placed in VIIB or 17th			ᇤ		ground state:		d > 3477	_
14.	Hydrogen bonding is pre					(a) BCl <sub>3</sub>		( ) J	Ц
	(a) H <sub>2</sub> O		(b) H <sub>2</sub> S		١.	(c) PCl <sub>3</sub>		(d) BeF <sub>2</sub>	
1.5	• • •		(d) HCl		4.				_
15.	Among the following ion					(a) with increasing bond			
			(b) $[Fe(H_2O)_6]^{2+}$		1	(b) with increasing exter			
	(c) $[Cu(H_2O)_6]^{2+}$		(d) $[Zn(H_2O)_6]^{2+}$		1	(c) with decrease in bor		_	
16.	Of the following, the m	etals	that cannot be obtained	l by		(d) from a single bond t		-	
	electrolysis of aqueous so			•	5.	The names which are as	socia	ated with ore dressing are	
	(a) Ag		(b) Mg			(a) hydraulic		(b) froth floatation	
	(c) Cu		(d) Al			(c) cupellation		(d) smelting	
17.	The elements which exist		• •	iture	6.	NaOH cannot be stored	in:	•	
	are:	,	<b>.</b>			(a) Al vessel		(b) zinc vessel	
	(a) Na		(b) Br			(c) glass vessel		(d) PVC vessel	
	(c) Hg		(d) Ga		7.	Which liberate Cl2 gas w	vith I	HCl?	
18.	White phosphorus (P <sub>4</sub> ) h		(-)		1	(a) KMnO <sub>4</sub>		(b) K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	
	(a) six P—P single bonds		(b) four P—P single bond	is 🗆		(c) MnO <sub>2</sub>		(d) KI	
	(c) four lone pairs of ele				8.	Fe can displace which o	f the	following ions from their	r salts
	(d) PPP angle of 60°				1	solutions?		•	
19.	NO <sub>2</sub> is obtained by heati	ng:				(a) Na <sup>+</sup>		(b) $Zn^{2+}$	
	(a) AgNO <sub>3</sub>		(b) Cu(NO <sub>3</sub> ) <sub>2</sub>		1	(c) Ag <sup>+</sup>		(d) Cu <sup>2+</sup>	
·	(c) KNO <sub>3</sub>		(d) NaNO <sub>3</sub>		9.			* *	
20.			(4) 1.141.03	_	1	(a) Na <sub>2</sub> O		(b) Al <sub>2</sub> O <sub>3</sub>	
	(a) NH <sub>4</sub> <sup>+</sup>		(b) BO <sub>3</sub> <sup>3</sup> -			(c) $SnO_2$		(d) CaO	
	(c) C <sub>2</sub> H <sub>4</sub>		(d) SO <sub>4</sub> <sup>2</sup>		10.			lue of hydration energy is	
21	Inert pair effect is shown		(u) 304		10.	(a) Li <sup>+</sup>		(b) Na <sup>+</sup>	
21.	(a) Pb	-	(b) Tl			(c) K <sup>+</sup>		(d) Cs <sup>+</sup>	
	(c) Ra		(d) Bi		11.		_	, ,	ii
22	, -				1 ***	(a) $ns^2$ electronic config			
LL.	Heating of oxalic acid wi			s:		(b) electropositive natural		ion	
	(a) CO		(b) CO <sub>2</sub> (d) SO <sub>3</sub>			(c) reducing nature			
22	(c) SO <sub>2</sub>					(d) found in nature		,	
۷3.	Xenon forms compound conditions. The known fi			PICIII	12	Concentrated sulphuric	hine	ie.	ئسا
				П	12.	(a) efflorescent			
	(a) XeF (c) XeF <sub>4</sub>		(b) XeF <sub>2</sub> (d) XeF <sub>3</sub>		ı			(b) hygroscopic	
	(U) ACFA	ப	(U) ACE3	LJ		(c) oxidising agent	$\Box$	(d) sulphonating agent	$\Box$

13.	Which are characteristic properties of carbon?	1	(c	) Carbon dioxide is one of the main chemical species
	(a) Catenation			responsible for it
	(b) Largest number of compounds		(d	) $CH_4$ , $O_3$ and CFC also contribute to greenhouse effect $\Box$
	(c) Most abundant element		Set 3	
	(d) Multiple bond formation			ick the correct statement(s) about the complex ion
14.	Ammonium compounds used as nitrogen fertilizers are:	1		$\left[\operatorname{Cu}(\mathrm{NH}_3)_4\right]^{2+}$ :
	(a) ammonium sulphate			
	(c) ammonium carbonate \( \square\) (d) urea			) $Cu^{2+}$ in the complex is $dsp^2$ hybridized
15.	Which decompose on heating?			) $Cu^{2+}$ in the complex is $sp^3$ hybridized $\Box$
	(a) $K_2CO_3$ $\square$ (b) $MgCO_3$		•	) the complex is square planar $\Box$
	(c) NaHCO <sub>3</sub>			) the complex is tetrahedral $\Box$
16.	Which statement(s) is/are correct?			he complex(es) which has/have 'd' electrons in the central
	(a) Radon is obtained from radium			etal atom is/are:
	(b) Argon is most abundant noble gas in atmosphere			) $MnO_4$ $\Box$ (b) $[Co(NH_3)_6]^{3+}$ $\Box$
	(c) Monazite is a source of neon			$ [Fe(CN)_6]^{3-} \qquad \qquad \Box  (d) \ [Cr(H_2O)_6]^{3+} \qquad \qquad \Box $
	(d) Helium is present in natural gas		3. K	<sub>4</sub> Fe(CN) <sub>6</sub> is used in detecting:
17.	Available chlorine is liberated from bleaching powder wh	_	(a	) $Ca^{2+}$ ions $\Box$ (b) $Fe^{2+}$ ions $\Box$
	it:			Fe <sup>3+</sup> ions $\Box$ (d) Cu <sup>2+</sup> ions $\Box$
	(a) is heated		•	Thich of the following statements are true for Mohr's salt?
	(c) reacts with alkali $\Box$ (d) reacts with $CO_2$			i) It decolourises KMnO <sub>4</sub> solution
18.	The common semiconductors are:			b) It is a double salt
10.	(a) C		-	The oxidation state of iron in it is $+2$
	(c) Ge		,	l) It is a primary standard
19.	Peroxy acids of sulphur are:	_		esonance structures of a molecule should have:
	(a) $H_2S_2O_8$ $\square$ (b) $H_2SO_5$			a) identical arrangements of atoms
	(c) $H_2S_2O_7$			b) nearly the same energy content
20.	Which of the following does/do not impart characteristics			e) the same number of unpaired electrons
20.	colour to the flame?	Sirc		i) different arrangement of atoms
	(a) MgSO <sub>4</sub>		1	he correct statements are:
	(c) $Sr(NO_3)_2$ $\square$ (d) $BaCl_2$			a) Generally the calcination and roasting is done in blast
21.		_	`	furnace
21.	mixture of NaCl and K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> is gently warmed v		(t	b) The sandy and rocky materials associated with ore are
	concentrated H <sub>2</sub> SO <sub>4</sub> ?	ATTI	,	called matrix
			((	e) Froth floatation process is suitable for sulphide ores
	(a) A deep red vapour is evolved			1) Substance that reacts with gangue to form fusible mass
	(b) Chlorine gas is evolved		`	is called slag
	(c) Chromyl chloride is formed		7. C	Consider the electronic configurations for neutral atoms,
	(d) The vapour when passed through NaOH solution gi		()	A) $1s^2$ , $2s^22p^6$ , $3s^1$
22	a yellow solution of Na <sub>2</sub> CrO <sub>4</sub>		Ì	B) $1s^2$ , $2s^22p^6$ , $3s^23p^6$ , $4s^2$ C) $1s^2$ , $2s^22p^6$ , $3s^23p^5$
22.	Amongst the following, identify the species with an at	iom	ì	$(2) 1s^2, 2s^22p^6, 3s^23p^5$
	+ 6 oxidation state: (a) $MnO_4$	_		Which of the following statements are true?
	17 19			a) (A) and (B) are metals while (C) is a nonmetal
	(c) $NiF_6^{2-}$			b) (A) and (B) are s-block elements while (C) is a p-block
23.	Which of the following are paramagnetic?		' '	element
	(a) $[Fe(CN)_6]^4$		((	c) The I.P. of (A) is higher than I.P. of (C)
	(c) $[NiCl_4]^{2-}$		3	d) (A), (B) and (C) are representative elements $\Box$
24.	Which of the following are coordination isomers	of		Which of the following species do not exist?
	[Cr(NH3)6][Co(CN)6]?		•	a) $Al_2Cl_6$ $\Box$ (b) $BH_3$ $\Box$
	(a) $[Co(NH_3)_6][Cr(CN)_6]$			$\begin{array}{cccc}  & & & & & & & & & & & \\  & & & & & & &$
	(b) [Cr(NH <sub>3</sub> ) <sub>4</sub> (CN) <sub>2</sub> ][Co(NH <sub>3</sub> ) <sub>2</sub> (CN) <sub>4</sub> ]		1 '	Dolomite is a mineral of:
	(c) [Cr(NH <sub>3</sub> ) <sub>3</sub> (CN) <sub>3</sub> ] [Co(NH <sub>3</sub> ) <sub>3</sub> (CN) <sub>3</sub> ]			
				a) Al
25	(d) All of the above What are correct about greenhouse warming?	Ш	,	
43.	(a) It results in global warming	<u> </u>		Which of the following is/are basic hydride(s)?
			1	a) HCl
	(b) It results in lowering levels of ocean over the years		. (	c) $H_2S$ $\square$ (d) $PH_3$ $\square$

11.	Which of the compound(s) is/are not soluble in water?	Ι	24.	Ammonia on reaction with hypochlorite anion can form:
	(a) NaCl $\Box$ (b) BaSO <sub>4</sub> $\Box$			(a) NO $\Box$ (b) NH <sub>4</sub> Cl $\Box$
	(c) $\text{Li}_2\text{CO}_3$ $\square$ (d) $\text{CaCO}_3$ $\square$			(c) $N_2H_4$ $\Box$ (d) $HNO_2$ $\Box$
12.	Which of the following reagents can oxidise KI to iodide?	1	25.	Which of the metal oxides are reduced by CO to give the
	(a) $H_2O_2/HC1$ $\Box$ (b) $O_3/H_2O$ $\Box$			corresponding metals?
	(c) $CuSO_4$ $\Box$ (d) $O_2$ $\Box$	1		(a) $ZnO$ $\Box$ (b) $CaO$ $\Box$
13.	Which of the following do pertain to biosphere?			(c) $Na_2O$ $\square$ (d) $Fe_2O_3$ $\square$
	(a) Hydrosphere $\Box$ (b) Lithosphere $\Box$		Set 4	4
	(c) Atmosphere $\Box$ (d) Thermosphere $\Box$		1.	Which of the following is/are outer orbital complex(es)?
14.	30 volume hydrogen peroxide means:		٠.	(a) $[Ni(NH_3)_6]^{2+}$ $\Box$ (b) $[Co(NH_3)_6]^{3+}$ $\Box$
	(a) 1 mL of solution liberates 30 mL of $O_2$ at N.T.P.	1		2.
	(b) 9.1 g $H_2O_2$ presents in 100 mL of $H_2O_2$		2	( ) 2 ( ) 2 ( ) 03
	(c) $30\%$ H <sub>2</sub> O <sub>2</sub> solution		2.	Identify the complexes which are expected to be coloured:
	(d) 30 mL of solution contains 1 mole of $H_2O_2$			(a) $[Ti(NO_3)_4]$ $\Box$ (b) $[Cu(NCCH_3)_4]^{\dagger}BF_4^{-}$ $\Box$
15.	Which statements are false?			(c) $[Cr(NH_3)_6]Cl_3$ $\square$ (d) $K_3[VF_6]$ $\square$
	(a) Manufacture of NaOH is done by Solvay's process		3.	Which of the following statements are wrong?
	(b) Manufacture of K <sub>2</sub> CO <sub>3</sub> is done by Solvay's process □	- 1		(a) $Hg_2Cl_2$ is called corrosive sublimate
	(c) Manufacture of NaHCO <sub>3</sub> is done by Solvay's process			(b) Hg <sub>2</sub> Cl <sub>2</sub> gives white precipitate with ammonium
				hydroxide
	(d) Manufacture of NaOH is done by Nelson cell	ı		(c) $Hg_2Cl_2$ is soluble in water
16.				(d) Hg <sub>2</sub> Cl <sub>2</sub> is used as purgative
	periodic table. Astatine would be expected to be:		4.	Addition of high proportions of manganese makes steel
	(a) more electronegative than iodine			useful in making rails of railroads because manganese:
	(b) composed of diatomic molecules			(a) gives hardness to steel
	(c) a solid at room temperature			(b) helps the formation of oxides of iron
	(d) limited to only – 1 oxidation state			(c) can remove oxygen and sulphur
17.	Which species are paramagnetic?	-	5	(a) this show inglies contained state of the
	(a) $CIO_2$ $\Box$ (b) $CIO_3$		Э.	Correct statements regarding bonding molecular orbitals are:
	(c) $CIF_3$ $\Box$ (d) $BrO_2$			(a) These possess less energy than combining atomic orbitals
18.	Aluminium is used:			(b) These have high electron density between the two
	(a) in thermite welding			nuclei
	(b) as an oxidiser in metallurgy	1		(c) These are formed when the lobes of the combining
	(c) for making utensils (d) in silvery paints	ıl		atomic orbitals have same sign
19.				(d) These have low electron density
	(a) Calcium cyanamide on treatment with steam forms NH	, l	6	$K^+$ , Ar, $Ca^{2+}$ and $S^{2-}$ have:
	and CaCO <sub>3</sub>	í	0.	(a) same number of electrons
-	(b) PCl <sub>5</sub> is kept in well stoppered bottles because it reacts	,		(b) same electronic configuration
	with moisture			(c) same ionisation potential
	(c) Ammonium nitrite on heating gives ammonia and nitrous	3		(d) same atomic radii
	acid $\Box$	]	7.	
	(d) $N_3H$ is a basic hydride	]		(a) Fifth period is the longest period
20.	Hydrogen sulphide exhibits:			(b) Among all the elements, chlorine has the highest
	(a) acidic properties $\Box$ (b) basic properties $\Box$			electronegativity
	(c) oxidising properties $\square$ (d) reducing properties $\square$	1		(c) Metallic character increases on going down the group
21.	Ionic radii of:			
	(a) $Ti^{4+} < Mn^{2+}$	]		(d) Lithium is the highest metal $\Box$
	(c) $K^+ > Cl^-$	] [	8.	CO <sub>2</sub> molecule is isostructural with:
22.	Which of the following elements do not occur in nature bu	t		(a) $HgCl_2$ $\Box$ (b) $SnCl_2$ $\Box$
	have been prepared artificially?			(c) $C_2H_2$ $\Box$ (d) $NO_2$ $\Box$
	(a) Ra		9.	Liquation process may be applied for the purification of:
	(c) Tc $\square$ (d) Pm $\square$	- 1		(a) copper $\Box$ (b) tin $\Box$
23.	Which of the following carbides on treatment with water give	e		(c) iron $\Box$ (d) lead $\Box$
	methane?	_	10.	When zeolite, which is hydrated sodium aluminium silicate
	(a) $Cu_2C_2$ $\square$ (b) $Be_2C$			is treated with hard water, the sodium ions are exchanged
	(c) $Al_4C_3$ $\Box$ (d) $Mg_2C_3$	] [		with:

**31.** (d)

**32.** (b)

**33.** (c)

**34.** (b)

**35.** (d)

	(a) Ca <sup>2+</sup> ions	□ (b) M	$1g^{2+}$ ions			(d) W	hen Al is heat	ed with p	otassium	hydroxid	de sol	lution,
	(c) H <sup>+</sup> ions	□ (d) S	$O_4^{2-}$ ions		•	hy	drogen is evol	lved	,		•	
11.	• •			copic?	19.	The r	eaction of sodi					s:
	(a) Washing soda		Caustic soda				dium sulphite		(b) sodiur			
	(c) Caustic potash	□ (d) C	Calcium chloride	• 🗆			odium iodide		(d) sodiur			ie 🗆
12.	Which of the follow		ial carbides?		20.		h of the follow					
	(a) ZrC	□ (b) V	/C				halogen which	ch is lic	juid at ro	om ter	npera	ture—
	(c) WC	□ (d) C	CaC <sub>2</sub>				romine					
13.	Nitrogen (I) oxide o	an be produced	by:		*		he most electro					
	(a) thermal decomp	osition of ammo	onium nitrate			(c) T	he halogen hav	ing highe	st electron	affinity	/Ch	dorine
	(b) thermal decomp	osition of ammo	nium nitrite						<b></b>			ᆜ
	(c) reaction of hydr	oxylamine and	nitrous acid		21		he strongest ox					, 🗆
	(d) thermal decomp	osition of ammo	nium dichroma	ate 🗆	21.		h of the follow	ing nyori	dization re	esults in	non-	pıanar
14.						orbita		_	(h) Jan <sup>2</sup>			П
	(a) Thermal power					(a) sp (c) sp	2		(b) $dsp^2$ (d) $dsp^3$			
	(c) Nuclear power p				22.	Which	h of the follow			ma alan	aont?	
15.	Which are used for				Lebe.		nnilquadium		(b) Rf	ilie eien	iciit :	
	(a) Limestone	□ (b) (	•			(c) K		<u></u>	(0) 14			
	(c) Alumina		Gypsum				Il the above are	e differen	t .			
16.	•						: The IUPAC na		*	th atomic	. numi	
	(a) lower the meltin			. 🗖		TANAME	is unnilquadiur					
	(b) increase the ele		vity				its Russian na				Oldidi.	it willio
	(c) minimise the ele				23.	Whic	h of the follo		-		ssive	when
17	(d) remove impuriti			ш			ed in conc. HN	_		- P-	052,4	
17.	Which of the follow  (a) The lattice struct			a different		(a) C			(b) Fe			
	(a) The lattice struc	inte of mainoid	and grapinic an			(c) C			(d) Al			
	(b) Graphite is hard	ler than diamon	ď		24.	Boro	n halides are:					
	(c) Graphite conduction			1		(a) E	lectron deficier	nt compo	unds			
	(d) Carbon in graph						ewis acids					
	is sp <sup>3</sup> hybridize						ewis bases					. 🗆
18.	Identify the correct						onic compound					
	(a) FeSO <sub>4</sub> ·(NH <sub>4</sub> ) <sub>2</sub> Se		d alum		25.		gases involved	in the fo	rmation of	photoc	hemic	cal fog
	(b) The mixture N	$1H_4NO_3 + Al$	powder is us	ed as an		are:	<b>v</b>	<b></b> 1	(h) (h)			
	explosive					(a) C			(b) SO <sub>2</sub>		_	ᆸ
	(c) Anhydrous AlC	$\mathfrak{l}_3$ is obtained v	vhen HCl is pa			(c) N	O	Ц	(d) Hydro	ocarbon	S	. 🗆
	aluminium							*				
		: .	ANSWERS	: OBJE	CTIV	E Q	UESTIONS			•		
Ty	pe 3 Multiple Choi	ce										
<b>(A)</b>	Cat 1											
(A)	Set 1		·									
	1. (a) 2. (c)	. 3. (c)	<b>4.</b> (a)	<b>5.</b> (d)	6.	(b)	<b>7.</b> (b)	8. (d)	9.	(d)	10.	(b)
	11. (b) 12. (a)	<b>13.</b> (c)	<b>14.</b> (b)	<b>15.</b> (c)	16.	(a)	17. (a)	<b>18.</b> (a)	19.	(d)	20.	(b)
	<b>21.</b> (b) <b>22.</b> (c)	<b>23.</b> (d)	<b>24.</b> (c)	25. (a)		(b)	<b>27.</b> (d)	<b>28.</b> (a)				(b)
	<b>31.</b> (c) <b>32.</b> (a)	33. (c)	<b>34.</b> (a)	<b>35.</b> (a)								
Set	· 2	•										
	1. (b) 2. (c)	3. (a)	<b>4.</b> (d)	<b>5.</b> (a)	6.	(b)	7. (c)	<b>8.</b> (a)	<b>9</b> .	(d)	10.	(d)
	11. (c) 12. (b)	13. (d)	14. (c)	15. (b)		(c)	17. (a)	18. (d)			20.	
	21. (a) 22. (b)	23. (c)	24. (a)	25. (d)		(c)	27. (b)	28. (d)			30.	
				, ,			• /					

(c) (a) (b) (b) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d
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(c)
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. (c)
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(a)
(a)
(b,d)
(a,d)
(a,b)
(a,b,c)

#### Type 4: Assertion-Reason type

The following questions consist of two statements each printed as Assertion (A) and Reason (R). Use the following key to choose the correct answer.

- (a) If both (A) and (R) are correct and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are correct but (R) is not the correct explanation of (A).
- (c) If (A) is correct but (R) is incorrect.
- (d) If (A) is incorrect but (R) is correct.
- (e) If both (A) and (R) are incorrect.
- 1. (A) Photochemical smog is produced by nitrogen oxides.
  - (R) Vehicular pollution is a major source of nitrogen oxides.
- (A) Lead tetraiodide (PbI<sub>4</sub>) is a stable compound.
  - (R) Iodide stabilizes higher oxidation state.

- 3. (A) HClO<sub>4</sub> is a stronger acid than HClO<sub>3</sub>.
  - (R) Oxidation states of Cl in  $HClO_4$  is + 7 and in  $HClO_3$ , it is + 5.
- 4. (A) The free gaseous chromium atom has six unpaired electrons.
  - (R) Half filled s-orbital has greater stability.
- 5. (A) Density of magnesium is less than of calcium.
  - (R) It is due to the presence of 3d-orbital.
- 6. (A) The first ionisation energy of Be is greater than that of B.
  - (R) 2p-orbital is lower in energy than 2s-orbital.
- 7. (A) F-atom has a less electron affinity than Cl-atom.
  - (R) Additional electrons are repelled more effectively by 3p electrons in Cl than by 2p electrons in F-atom.
- 3. (A) Sigma ( $\sigma$ ) is a strong bond while pi ( $\pi$ ) is a weak bond.
  - (R) Atoms rotate freely about pi  $(\pi)$  bond.
- (A) Stannous chloride is a powerful oxidising agent which oxidises mercuric chloride to metallic mercury.

- (R) Stannous chloride gives grey precipitate with mercuric chloride but stannic chloride does not do so.
- 10. (A) The fluorine has lower reactivity.
  - (R) F—F bond has low bond dissociation energy.
- 11. (A) Potassium and caesium are used in photoelectric cells.
  - (R) Potassium and caesium emit electrons on exposure to light.
- 12. (A) Diamond is a bad conductor.
  - (R) Graphite is a good conductor.
- 13. (A) Carbon tetrachloride is resistant towards hydrolysis, whereas silicon tetrachloride is readily hydrolysed.
  - (R) Silicon has bigger size and can accommodate large number of water molecules around itself.
- 14. (A) Diborane is an electron deficient.
  - (R) There are no enough valence electrons to form expected number of covalent bonds.
- 15. (A) The bond order in a molecule can have any value, positive or negative, integral or fractional or zero.
  - (R) The bond order of a molecule depends upon the number of electrons in the bonding and antibonding molecular orbitals.
- 16. (A) Chlorine and sulphur dioxide both are bleaching agents.
  - (R) The bleaching action of chlorine and sulphur dioxide is performed through the process of oxidation.
- (A) Copper reacts with hydrochloric acid and liberates hydrogen from the solution of dilute hydrochloric acid.
  - (R) Hydrogen is below copper in electrochemical series.
- 18. (A) Bond order can assume any value including zero.
  - (R) Higher the bond order, shorter is the bond length and greater is the bond energy.
- 19. (A) Beryllium and magnesium impart colour to the flame.
  - (R) Beryllium and magnesium both have big size and lower ionisation energies.
- (A) Carbon forms covalent compounds whereas lead forms ionic compounds.
  - (R) Carbon can lose electrons to form C4+ while lead cannot.
- 21. (A) The melting and boiling points of alkali metals are very high.
  - (R) Alkali metals have large size molecules.
- 22. (A) Molecular weight of oxygen is 16.
  - (R) Atomic weight of oxygen is 16.
- (A) Copper sulphate solution on reacting with excess of potassium cyanide solution gives K<sub>3</sub>[Cu(CN)<sub>4</sub>].
  - (R) Cupric state of copper is more stable than cuprous state in the complex.
- 24. (A) Alkali metals impart colour to the flame.
  - (R) Their ionisation energies are low.
- 25. (A) Bond angle in H<sub>2</sub>O is more than in NH<sub>3</sub>.
  - (R) Lone pair-lone pair repulsion > lone pair-bond pair repulsion.
- 26. (A) Bond dissociation energy of fluorine is less than that of chlorine.
  - (R) Electronegativity of fluorine is much higher than chlorine.
- (A) Potassium carbonate cannot be manufactured by a process similar to Solvay's process.
  - (R) Potassium hydrogen carbonate is soluble in water.
- 28. (A) Dioxygen is paramagnetic in nature.
  - (R) Oxygen is found in free state only.
- 29. (A) NO<sub>3</sub> is planar while NH<sub>3</sub> is pyramidal.
  - (R) N in NO<sub>3</sub> has  $sp^2$  and in NH<sub>3</sub> has  $sp^3$  hybridisation.
- 30. (A) Carbonates and hydroxides are concentrated by froth floatation
  - (R) In froth floatation process pine oil is used because it preferentially wets the ore particles.
- 31. (A) D<sub>2</sub>O is called hard water.
  - (R) It's degree of dissociation is high.
- (A) The alkali metals can form ionic hydrides which contain the hydride ion, H<sup>-</sup>.

- chloride (R) The alkali metals have low electronegativity. Their hydrides conduct electricity when fused and liberate hydrogen at the anode.
  - 33. (A) Na<sub>2</sub>SO<sub>4</sub> is soluble in water while BaSO<sub>4</sub> is insoluble.
    - (R) Lattice energy of barium sulphate exceeds its hydration energy.
  - 34. (A) H<sub>2</sub>O is the only hydride of chalcogens which is liquid at ordinary temperature.
    - (R) In ice each O-atom is surrounded by two covalent bonds and two H-bonds.
  - 35. (A) Xenon forms fluorides.
    - (R) Because 5d-orbitals are available for valence shell expansion.
  - 36. (A) Pb<sup>4+</sup>can be reduced easily to Pb<sup>2+</sup>.
    - (R) The size of Pb2+ is bigger than Pb4+ as a second of the size of Pb2+ is bigger than Pb4+ as a second of the size of Pb2+ is bigger than Pb4+ as a second of the size of Pb2+ is bigger than Pb4+ as a second of the size of Pb2+ is bigger than Pb4+ as a second of the size of Pb2+ is bigger than Pb4+ as a second of the size of Pb2+ is bigger than Pb4+ as a second of the size o
  - 37. (A) CO<sub>2</sub> and SiO<sub>2</sub> have same physical state at room temperature.
    - (R) CO₂ contains C=O bonds but SiO₂ does not contain S=O bonds.
  - 38. (A) Tungsten has a very high melting point.
    - (R) Tungsten is a covalent compound.
  - 39. (A) Iron compounds are paramagnetic and coloured.
    - (R) Iron in Fe<sup>2+</sup> or Fe<sup>3+</sup> does not contain unpaired electrons.
  - 40. (A) Every d-block series consists ten elements.
    - (R) Because, the maximum capacity of d-subshell is of ten electrons, d-subshell is gradually filled up.
  - 41. (A) Sulphuric acid is more viscous than water.
    - (R) In H<sub>2</sub>SO<sub>4</sub>, the S-atom exhibits its highest oxidation state.
  - 42. (A) Sulphur dioxide can act as oxidising as well as reducing agent.
    - (R) In sulphur dioxide S assumes  $sp^3d$  hybrid states.
  - 43. (A) H<sub>3</sub>PO<sub>3</sub> is a monobasic acid.
    - (R) Two H-atoms are directly attached to P.
  - 44. (A) Carbon monoxide reacts with nickel to form nickel carbonyl.
    - (R) Carbon monoxide is an acidic oxide.
  - 45. (A) Zinc, cadmium and mercury do not show characteristic properties of transition metals.
    - (R) In these metals outermost shell is completely filled.
  - 46. (A) FeS<sub>2</sub> is known as fool's gold.
    - (R) FeS<sub>2</sub> has yellow metallic appearance.
  - 47. (A) Lanthanides are generally diamagnetic.
    - (R) Lanthanides have the tendency to attain +3 oxidation state.
  - 48. (A) EAN of Fe in its complexes is always 36.
    - (R) Oxidation state of Fe in Fe(CO)<sub>5</sub> is +2.
  - 49. (A) Chelates are less stable than ordinary coordination compounds.
    - (R) Chelates can be formed by bidentate ligands.
  - 50. (A) Ionic compounds tend to be non-volatile.
    - (R) Ionic compounds are bad conductors in solid state.
  - (A) Reaction of SO<sub>2</sub> and H<sub>2</sub>S in presence of Fe<sub>2</sub>O<sub>3</sub> catalyst gives elemental sulphur.
    - (R) SO<sub>2</sub> is a reducing agent.
  - 52. (A) Addition of NH<sub>4</sub>OH to an aqueous solution of BaCl<sub>2</sub> in presence of NH<sub>4</sub>Cl(excess) precipitates Ba(OH)<sub>2</sub>.
    - (R) Ba(OH)<sub>2</sub> is insoluble in water.
  - 53. (A) First ionisation energy of fluorine is lower than oxygen.
    - (R) Across a period effective nuclear charge decreases.
  - 54. (A) Borax bead test is not suitable for Al(III).
    - (R) Al<sub>2</sub>O<sub>3</sub> is insoluble in water.
  - 55. (A) Potassium ferricyanide is paramagnetic while potassium ferrocyanide is diamagnetic.
    - (R) Crystal field splitting in ferrocyanide ion is greater than in ferricyanide ion.
  - 56. (A) Molecular nitrogen is less reactive than molecular oxygen.
    - (R) The bond length of N<sub>2</sub> is shorter than that of oxygen.
  - 57. (A) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is used as primary standard in volumetric analysis.
    - (R) It has a good solubility in water.

#### Assertion-Reason Type

1. (b)	<b>2.</b> (e)	<b>3.</b> (b)	<b>4.</b> (c)	5. (e)	<b>6.</b> (a)	<b>7.</b> (c)	8. (c)	<b>9.</b> (d)	<b>10.</b> (d)
<b>11.</b> (a)	<b>12.</b> (b)	<b>13.</b> (b)	<b>14.</b> (a)	<b>15.</b> (a)	<b>16.</b> (c)	<b>17.</b> (e)	18. (b)	<b>19.</b> (e)	<b>20.</b> (c)
<b>21.</b> (d)	<b>22.</b> (d)	<b>23.</b> (c)	<b>24.</b> (a)	<b>25.</b> (d)	<b>26.</b> (b)	<b>27.</b> (a)	<b>28.</b> (c)	<b>29.</b> (a)	<b>30.</b> (d)
<b>31.</b> (e)	<b>32.</b> (a)	<b>33.</b> (a)	<b>34.</b> (b)	<b>35.</b> (a)	<b>36.</b> (b)	<b>37.</b> (d)	<b>38.</b> (c)	<b>39.</b> (c)	<b>40.</b> (a)
<b>41.</b> (b)	<b>42.</b> (c)	<b>43.</b> (e)	<b>44.</b> (c)	<b>45.</b> (c)	<b>46.</b> (a)	<b>47.</b> (d)	<b>48.</b> (e)	<b>49.</b> (d)	<b>50.</b> (b)
<b>51.</b> (b)	<b>52.</b> (e)	<b>53.</b> (e)	<b>54.</b> (b)	<b>55.</b> (c)	<b>56.</b> (b)	<b>57.</b> (c)			

Type 5: Thought Type Questions

#### Thought 1

In the modern periodic table, the elements are placed in order of increasing atomic number. The long form of periodic table shows all the elements in numerical order. The start of a new period always corresponds to the introduction of the first electron into the s-orbital of a new principal quantum number. The number of elements in each period corresponds to the number of electrons required to fill the orbitals according to aufbau principle.

1s, 2s2p, 3s3p, 4s3d4p, 5s4d5p, 6s4f5d6p, 7s5f6d7p.

The main groups correspond to elements in which s and p orbitals are being filled. The transition elements are those in which d-orbitals are being filled. Each group contains elements of similar electronic configuration. According to the recommendations of IUPAC, the groups of elements are numbered from 1 to 18. The elements corresponding to filling of 4f-orbitals are called lanthanons and those corresponding to the filling of 5f-orbitals are called actinons. These elements are accommodated into two separate horizontal rows below the table.

There are only 81 stable elements known. For these elements, one or more isotopes do not undergo spontaneous radioactive decay. No stable isotope exists for any element above bismuth. Two elements, uranium and thorium, for which only radioactive isotopes exist, are found quite abundantly on earth because the half-lives of some of their isotopes are almost as great as the age of earth.

- ..... periods and ..... groups are there in the long form of the periodic table.
  - (a) 7 and 16
- (b) 7 and 9
- (c) 7 and 18
- (d) 9 and 9
- Configuration of the final elements of 3d, 4d, 5d series respectively are:
  - (a)  $3d^54s^2$ ,  $4d^{10}5s^2$ ,  $5d^{10}6s^2$
  - (b)  $3d^{10}4s^2$ ,  $4d^{10}5s^2$ ,  $5d^{10}6s^2$
  - (c)  $3d^{10}4s^2$ ,  $4d^{10}5s^1$ ,  $5d^{10}6s^1$
  - (d)  $3d^94s^2$ ,  $4d^{10}5s^2$ ,  $5d^{10}6s^1$
- Two elements, one belonging to 4d series and other to lanthanon series, which are not stable and not found in nature and have been discovered by artificial means are:
  - (a) Tc and Eu
- (b) Nb and Gd
- (c) Y and Dy
- (d) Tc and Pm
- Outermost configuration of two p-block elements A and B are  $ns^2np^1$  and  $ns^2np^6$  respectively. The elements are if n=4:

- (a) A = Ga, B = Xe
- (b) A = In, B = Xe
- (c) A = Ga, B = Kr
- (d) A = Zn, B = Kr
- General outermost electronic configuration of the elements situated above and below X (Atomic number = 50) would
  - (a)  $ns^2np^2$
- (c)  $ns^2np^4$
- (b)  $ns^2np^3$ (d)  $ns^2np^5$

#### Thought 2

Quantum mechanical calculations show that mathematical mixing of certain combinations of orbitals in a given atom gives rise to new atomic orbitals. The spatial orientations of these new orbitals lead to more stable bonds and are consistent with the observed molecular shapes. The process of orbital mixing is called hybridization and the new atomic orbitals are called hybrid orbitals. Two key points about the number and type of the hybrid orbitals are that:

- (i) The number of hybrid orbitals obtained equals the number of atomic orbitals mixed.
- (ii) The type of hybrid orbitals obtained varies with the type of atomic orbitals mixed.

The following two methods are used to know about the type of hybridization in the molecule.

Method 1: Count number of atoms directly attached to central atom + lone pairs + single electrons

Method 2 : Count  $\sigma$  bonds + coordinate bonds + lone pairs + single electrons

If the number comes out to be:

- $5 \longrightarrow sp^3d$  hybridization  $2 \longrightarrow sp$  hybridization
- $3 \longrightarrow sp^2 \text{ hybridization}$   $3 \longrightarrow sp^2 \text{ hybridization}$   $4 \longrightarrow sp^3d^2 \text{ hybridization}$  $d^2sp^3$  hybridization  $4 \longrightarrow sp^3$  hybridization

dsp<sup>2</sup> hybridization

1. The hybridization scheme for central atom includes a d-orbital contribution in:

(a)  $I_3^-$ 

(b) PCl<sub>3</sub>

(c)  $NO_3$ 

- (d) H<sub>2</sub>Se
- 2. Hybrid states of Xe in XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub> respectively are: (b)  $sp^3d$ ,  $sp^3d^2$ ,  $sp^3d^3$ 
  - (a)  $sp^2$ ,  $sp^3d$ ,  $sp^3d^2$ (c)  $sp^3d^2$ ,  $sp^3d$ ,  $sp^3d^3$
- (d)  $sp^2$ ,  $sp^3$ ,  $sp^3d$
- 3. Phosphorus pentachloride in gaseous state exists as a monomer. In solid state, it exists as PCl<sub>4</sub> and PCl<sub>6</sub> ions. The hybrid state of P atom in PCl<sub>5</sub> is  $sp^3d$ . The hybrid states of P atoms in PCl<sub>4</sub> and PCl<sub>6</sub> will be respectively:

#### Miscellaneous

- (a)  $sp^3d$ ,  $sp^3d^2$ (c)  $sp^3$ ,  $sp^3d^2$
- (b)  $sp^{3}$ ,  $sp^{3}d$ (d)  $sp^{3}d^{2}$ ,  $sp^{3}d$

- 4. The hybrid states of central atoms in NO<sub>2</sub>, NO<sub>2</sub> and NH<sub>4</sub>
  - (a)  $sp^3$ ,  $sp^2$ ,  $sp^3d$  respectively (b)  $sp^3$ ,  $sp^2$ ,  $sp^3$  respectively (c)  $sp^2$ ,  $sp^3$ ,  $sp^3$  respectively (d) sp,  $sp^2$ ,  $sp^3$  respectively
- 5. The hybrid states of carbon in diamond, graphite and acetylene respectively are:
  - (a)  $sp^2$ , sp,  $sp^3$ (c)  $sp^3$ ,  $sp^2$ , sp
- (b) sp,  $sp^2$ ,  $sp^3$ (d)  $sp^2$ ,  $sp^3$ , sp

## Thought 3

 $CuSO_4 \cdot 5H_2O + KCN (excess) \longrightarrow A (cyano complex)$  $CuSO_4.5H_2O + NH_4OH (excess) \longrightarrow B (ammine complex)$ 

- 1. The formulae of A and B are :
  - (a) K<sub>2</sub>[Cu(CN)<sub>4</sub>], [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>
  - (b) K<sub>3</sub>[Cu(CN)<sub>4</sub>], [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>
  - (c) K[Cu(CN)<sub>2</sub>], [Cu(NH<sub>3</sub>)<sub>6</sub>]SO<sub>4</sub>
  - (d) K<sub>3</sub>[Cu(CN)<sub>6</sub>], [Cu(NH<sub>3</sub>)<sub>6</sub>]SO<sub>4</sub>
- **2.** The IUPAC name of A and B are:
  - (a) potassium cupro cyanide, tetraammine cupric sulphate
  - (b) tetracyanopotassium cuprate(I), hexaammine copper(II) sulphate
  - (c) potassium tetracyano cuprate(I), tetraammine copper(II)
  - (d) potassium tetracyanocopper(I), tetraammine cuprate(II) sulphate
- 3. The hybridized state of copper in A and B are:
  - (a)  $sp^3$ ,  $dsp^2$ (c)  $dsp^2$ ,  $dsp^2$
- (b)  $sp^{3}$ ,  $sp^{3}$
- (d)  $sp^3d^2$ ,  $d^2sp^3$
- 4. Predict the magnetic nature of A and B:
  - (a) Both are diamagnetic
- (b) Both are paramagnetic
- (c) A is paramagnetic and B is diamagnetic
- (d) A is diamagnetic and B is paramagnetic
- 5. In the formation of complex A, which gas is evolved?
  - (a)  $H_2$
- (b) O<sub>2</sub>
- (c) HCN
- (d)  $(CN)_2$

## Thought 4

Colemanite + (A) 
$$\longrightarrow$$
 Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>  
Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> + (B)  $\longrightarrow$  H<sub>3</sub>BO<sub>3</sub>  
H<sub>3</sub>BO<sub>3</sub>  $\xrightarrow{\text{Strongly} \atop \text{heated}}$  (C)

- 1. The formula of the colemanite mineral is:
  - (a) Ca<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·5H<sub>2</sub>O
- (b) CaB<sub>4</sub>O<sub>7</sub>·NaBO<sub>2</sub>·8H<sub>2</sub>O
- (c) 2Mg<sub>3</sub>B<sub>8</sub>O<sub>15</sub>·MgCl<sub>2</sub>
- (d) Ca<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·3H<sub>2</sub>O

- **2.** The compound (A) is:
  - (a) sodium carbonate
- (b) sodium oxide
- (c) sodium sulphate
- (d) carbon dioxide
- **3.** The compound (B) is:
  - (a) concentrated HCl
- (b) concentrated H<sub>2</sub>SO<sub>4</sub> (d) neither (a) nor (b)
- (c) either (a) or (b) **4.** The compound (C) is:
  - (a) B

(b)  $B_2O_3$ 

(c) BO<sub>2</sub>

- (d) BO<sub>3</sub>
- **5.** (*D*) and (*E*) are :
  - (a)  $H_2B_4O_7$ ,  $HBO_2$
- (b) HBO<sub>2</sub>, H<sub>2</sub>B<sub>4</sub>O<sub>7</sub>
- (c)  $H_4B_2O_5, H_2B_4O_7$
- (d)  $HBO_2$ ,  $H_5B_3O_7$
- 6. HBO3 is:
  - (a) Monobasic and weak Lewis acid
  - (b) Monobasic and weak Bronsted acid
  - (c) Monobasic and strong Lewis acid
  - (d) Tribasic and weak Bronsted acid

#### Thought 5

Potassium permanganate is the most important and well known salt of permanganic acid. It is prepared from pyrolusite ore. It is an oxidising agent in alkaline, neutral or acidic solutions. It is a purple coloured crystalline compound and fairly soluble in water.

- 1. Pyrolusite + KOH or  $K_2CO_3 = \frac{Fuscum an}{+ a little KNO_3}$ the product (A) is:
  - (a)  $Mn_3O_4$
- (b)  $Mn_2O_7$
- (c)  $K_2MnO_4$
- (d) KMnO<sub>4</sub>
- 2. The molecular mass of KMnO<sub>4</sub> is M. Its equivalent mass in acidic medium will be:
  - (a) M
- (b) M/2
- (c) M/3
- (d) M/5

3. For the redox reaction,

 $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O_3$ the correct coefficients of the reactants for the balanced reaction are:

]	$MnO_4^-$	$C_2O_4^{2-}$	$H^+$
(a)	2.	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

- 4. If equal volumes of 1M KMnO<sub>4</sub> and 1M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solutions are allowed to oxidise Fe(II) to Fe(III), then Fe(II) oxidised will be:
  - (a) more by KMnO<sub>4</sub>
- (b) more by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
- (c) equal in both cases
- (d) cannot be compared
- 5. KMnO<sub>4</sub> is used as an oxidising agent in volumetric analysis in acidic medium. The acidic medium is maintained by the use of:
  - (a) dilute HCl
- (b) dilute HNO<sub>3</sub>
- (c) dilute H<sub>2</sub>SO<sub>4</sub>
- (d) concentrated H<sub>2</sub>SO<sub>4</sub>

## ANSWERS

- Thought 1 2. (b) 3. (d) 4. (c) 5. (a) Thought 2 2. (b) 3. (c) **1.** (a) 4. (d) 5. (c) Thought 3 **1.** (b) **2.** (c) **3.** (a) 4. (d) 5. (d)
- Thought 4 1. (a) 2. (a) 3. (c) **4.** (b) **5.** (b) **6.** (a) Thought 5 1. (c) 2. (d) **3.** (a) **4.** (b) 5. (c)

# Practice Paper —1 ....

	SECTION: 1			(a) a 4 a a a b a a a a a a a a a a a a a a	
Ti quesi	ight Objective Type Questions	Each		Which of the following is linear? (a) $XeF_2$ $\Box$ (b) $XeF_4$	□ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □
	$\bigcirc B + H_2O \longrightarrow C$				
	$C + CO_2 \longrightarrow A \text{ (milky)}$			_ (0) 11	⊐
	$C + NH_4Cl \longrightarrow D \text{ (gas)}$		10.	The Correct order of magnetic moments amongst following	ıg
	$D + H_2O + CO_2 \longrightarrow E$			complex ions is:	
	$E + \text{NaCl} \longrightarrow F$			() [	Ш
	$F \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$			(1) [	
	D, $E$ and $F$ are :			(4) [1,11,11,11,11]	
	(a) NH <sub>3</sub> , NH <sub>4</sub> Cl, NH <sub>4</sub> HCO <sub>3</sub>			(d) $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$	
	(b) NH <sub>3</sub> , NH <sub>4</sub> HCO <sub>3</sub> , NaHCO <sub>3</sub>			•	
	(c) NH <sub>4</sub> HCO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> , NaHCO <sub>3</sub>		***************************************	SECTION: 2	
2.	(d) none of the above  An aqueous solution of ferrous aluminium sulphate			OLO HOIT . Z	
4.	chrome alum is heated with excess of $Na_2O_2$ and filtered. materials obtained are:  (a) a colourless filtrate and a green residue  (b) a yellow filtrate and a green residue  (c) a yellow filtrate and a brown residue  (d) a green filtrate and a brown residue  The bond angle in $H_2S$ is:  (a) same as that of $CI$ —Be— $CI$ in $BeCI_2$ (b) greater than $H$ — $N$ — $H$ bond angle in $NH_3$ (c) same as $CI$ — $SI$ — $CI$ in $SI$ $II$ (d) greater than $H$ — $SI$ e— $II$ and less than $II$ eact with water liberate $II$ ions along with $II$ 0 gas?  (a) $II$ 1 (b) $II$ 2 and $II$ 3 (c) $II$ 4 (d) $II$ 5 All of these which one of the following is not a protonic acid?  (a) $II$ 4 (d) $II$ 5 $II$ 6 (e) $II$ 7 (d) $II$ 8 $II$ 9 (e) $II$ 9 (e) $II$ 9 $II$ 9 (f) $II$ 9 $II$ 9 (f) $II$ 9 $II$ 9 (f) $II$ 9 $II$ 9 (f) $II$ 9 $II$ 9 (f) $II$ 9 $II$ 9 (f) $II$ 9 (f) $II$ 9 $II$ 9 (f) $II$ 9	er to	ques be a 11.	<ul> <li>(b) The hybridization of Xe in XeF<sub>4</sub> is sp<sup>3</sup>d<sup>2</sup></li> <li>(c) Among the noble gases, the occurrence of argon highest in the air</li> <li>(d) Liquid helium is used in cryogenic liquids</li> <li>(d) Liquid helium is used in cryogenic liquids</li> <li>(e) Which of the following are correct?</li> <li>(a) LiClO<sub>4</sub> &gt; NaClO<sub>4</sub> &gt; KClO<sub>4</sub> (solubility in water)</li> <li>(b) RbI &gt; RbBr &gt; RbCl &gt; RbF (lattice energy)</li> <li>(c) BaCO<sub>3</sub> &gt; SrCO<sub>3</sub> &gt; CaCO<sub>3</sub> &gt; MgCO<sub>3</sub> (thermal stability</li> <li>(d) Li<sup>+</sup> &gt; Be<sup>2+</sup> &gt; Na<sup>+</sup> &gt; Mg<sup>2+</sup> (hydration energy)</li> <li>(d) Li<sup>+</sup> &gt; Be contraction with the following species is/are isostructural with the followin</li></ul>	
6.	A red solid is insoluble in water. However, it becomes sol			IF <sub>4</sub> ?	
	if some KI is added to water. Heating the red solid in a tube results in the liberation of some violet coloured fu and droplets of a metal appear on the cooler parts of the tube. The red solid is:	ımes	14.	(a) $[Cu(NH_3)_4]^{2+}$ $\Box$ (b) $XeF_4$ $\Box$ (c) $BF_4^ \Box$ (d) $[Ni(CN)_4]^{2-}$ $\Box$ The elements which exist in liquid state at room temperaturare:	□ □ ure
	(a) $HgI_2$		ŭ.,	(a) Na $\Box$ (b) Hg	
7	(c) Pb <sub>3</sub> O <sub>4</sub>	. <del></del> .	1.0		
1.	The geometry of ICl <sub>2</sub> ions is:		15.	H <sub>2</sub> O <sub>2</sub> is obtained when dilute H <sub>2</sub> SO <sub>4</sub> reacts with:	
	(a) trigonal with $sp^2$ -hybridisation (b) tetrahedral with $sp^3$ -hybridisation				

#### **SECTION: 3**

#### Assertion-Reason Type Questions .....

Each question in this section contains Assertion (A) and **Reason** (R). Each question has four choices, out of which only one is correct. Mark your choice from the following options.

- (a) Both (A) and (R) are true and (R) is the correct explanation
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is correct but (R) is false.
- (d) (A) is false but (R) is ture.
- 16. (A) Halogens have maximum negative electron gain enthalpy in respective periods of the periodic table.
  - (R) Halogens have high effective nuclear charge.
- 17. (A) Between SiCl<sub>4</sub> and CCl<sub>4</sub>, only SiCl<sub>4</sub> reacts with water.
  - (R) SiCl<sub>4</sub> is ionic while CCl<sub>4</sub> is covalent.
- 18. (A) Smaller the size of an atom greater is its electronegativity.
  - (R) Electronegativity refers to the tendency of the atom to share electrons with the other atom.
- 19. (A) CaH<sub>2</sub> is known as hydrolith.
  - (R) It is an ionic hydride and on hydrolysis it evolves hydrogen.
- 20. (A) All noble gases are monoatomic.
  - (R) The electronic configuration of noble gases is either  $ns^2np^6$  or  $1s^2$  (helium).

#### **SECTION: 4**

#### Linked Comprehension Type Questions .....

This section contains a paragraph. Based upon paragraph, multiple choice questions have been given. Each question has 4 choices. Out of which only one is correct.

Molecular orbitals are formed by linear combination of atomic orbitals (LCAO). Two atomic orbitals can overlap forming two molecular orbitals, one of which lies at lower energy called bonding molecular orbital and other at higher energy called antibonding molecular orbitals. Pauli exclusion principle and Hund's rule are applicable for the filling of molecular orbitals. Molecules are said to be stable if number of electrons in bonding molecular orbitals are more than in the antibonding molecular orbitals. Molecular orbital theory can explain the magnetic behaviour of the molecules

21.	In a molecule, number of	of el	ectrons in bonding molecu	lar					
			electrons in the antibondi						
	molecular orbitals, hence:		ciculons in the unitodial	6					
	(a) a bond will be formed			П					
	(b) no bond will be formed								
	(c) information is not sufficient								
	(d) none of the above								
22.	Molecular orbital theory is	pref	erred over valence bond the	ory					
	as it can explain:								
	(a) bond strength		(b) geometry of molecule						
	(c) magnetic nature		(d) none of these						
23.	In which set of molecules	s, all	the species are paramagnet	ic?					
	(a) $B_2, O_2, N_2$		(b) $B_2$ , $O_2$ , $NO$						
	(c) $B_2, F_2, O_2$		(d) $B_2, O_2, Li_2$						
	SECT	ΓΙΟ	N:5						
	SECT		N:5						

#### Matrix-Match Type Questions .....

Each question contains statements given in two columns, which have to be matched.

24. Match List-II with List-II:

#### List-I List-II (Metal) (Procedure of extraction) (a) Iron (p) Carbon/carbon monoxide reduction method (b) Lead (a) Self reduction (c) Copper (r) Thermite process (d) Chromium (s) Hydrometallurgical process 25. Match Column-II with Column-II: Column-II

#### Column-I

- (a) Orthophosphorus acid
- (b) Sulphurous acid
- (c) Sulphuric acid
- (d) Perchloric acid
- (p) Monobasic acid
- (q) Dibasic acid
- (r) Oxidising agent
- (s) Reducing agent

## Practice Paper: 1 ....

1. (b)

$$\begin{array}{c} \text{CaCO}_{3} \longrightarrow \text{CaO} + \text{CO}_{2} \\ \text{(A)} \qquad \text{(B)} \\ \text{CaO} + \text{H}_{2}\text{O} \longrightarrow \text{Ca}(\text{OH})_{2} \\ \text{(C)} \\ \text{Ca}(\text{OH})_{2} + \text{CO}_{2} \longrightarrow \text{CaCO}_{3} + \text{H}_{2}\text{O} \\ \text{Milkiness} \\ \text{Ca}(\text{OH})_{2} + 2\text{NH}_{4}\text{Cl} \longrightarrow 2\text{NH}_{3} + \text{CaCl}_{2} + 2\text{H}_{2}\text{O} \\ \text{(D)} \\ \text{NH}_{3} + \text{H}_{2}\text{O} + \text{CO}_{2} \longrightarrow \text{NH}_{4}\text{HCO}_{3} \\ \text{(E)} \\ \text{NH}_{4}\text{HCO}_{3} + \text{NaCl} \longrightarrow \text{NaHCO}_{3} + \text{NH}_{4}\text{Cl} \\ \text{(F)} \\ 2\text{NaHCO}_{3} \longrightarrow \text{Na}_{2}\text{CO}_{3} + \text{CO}_{2} + \text{H}_{2}\text{O} \\ \end{array}$$

2. (c)

> Na<sub>2</sub>O<sub>2</sub> reacts with water and forms NaOH and H<sub>2</sub>O<sub>2</sub>. Sulphates of iron, aluminium and chromium are converted into corresponding hydroxides. Fe(OH)<sub>2</sub> is oxidised to Fe(OH)<sub>3</sub>, i.e., a brown insoluble precipitate. Al(OH)<sub>3</sub> dissolves forming NaAlO<sub>2</sub> (colourless) while Cr(OH)<sub>3</sub> is converted into Na<sub>2</sub>CrO<sub>4</sub> (yellow solution).

$$2Cr(OH)_3 + 4NaOH + 3O \longrightarrow 2Na_2CrO_4 + 5H_2O$$

3. (d)

> Bond angles in BeCl<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O and SnCl<sub>2</sub> are 180°, 106.5°, 104.5° and 119° respectively. O, S and Se belong to the same group and in their hydrides, there is  $sp^3$  hybridisation and bond angles of hydrides decrease down the group.

4. **(b)** 

$$O^{2-} + H_2O \longrightarrow 2OH^-$$
  
 $2O_2^{2-} + 2H_2O \longrightarrow 4OH^- + O_2$   
 $2O_2^- + 2H_2O \longrightarrow 2OH^- + H_2O_2 + O_2$ 

5. (a)

> B(OH)<sub>3</sub> does not act as a proton donor but behaves as a Lewis acid, i.e., it accepts a pair of electrons from OH ion.

$$B(OH)_3 + H \longrightarrow [B(OH)_4]^- + H^+$$

So, B(OH)<sub>3</sub> is not a protonic acid.

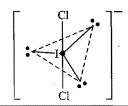
6.

HgI<sub>2</sub> dissolves in presence of KI forming a soluble complex.

$$\begin{array}{ccc} 2KI + HgI_2 & \longrightarrow & K_2HgI_4 \\ & & HgI_2 & \stackrel{Heat}{\longrightarrow} & Hg & + & I_2 \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & \\ & & & \\ & & \\ & & & \\ &$$

7.

 $ICl_2^-$  has linear shape. Iodine undergoes  $sp^3d$  hybridisation.



8. (a)

 $XeF_2$  is linear, xenon undergoes  $sp^3d$  hybridisation.

9.

The configuration of Cr is

$$1s^2$$
,  $2s^22p^6$ ,  $3s^23p^63d^5$ ,  $4s^1$ 

The Cr<sup>+</sup> ion has stable configuration and hence, requires more energy to remove an electron. Thus, the ionisation energy of Cr is highest amongst V, Mn and Fe.

10.

Greater the unpaired electrons, higher will be the paramagnetic character.

 $[MnCl_4]^{2-}$  5 unpaired electrons  $sp^3$ -hybridisation.  $[CoCl_4]^{2-}$  3 unpaired electrons  $sp^3$ -hybridisation.

 $[Fe(CN)_6]^{4-}$  no unpaired electron  $d^2sp^3$ -hybridisation.

11. (b, c, d)

XeO<sub>3</sub> has three  $\sigma$  and three  $\pi$ -bonds. Hence, this alternative is wrong.



12. (a, c)

13. (a, b, d)

	Hybridization	Structure
IF <sub>4</sub>	$sp^3d^2$	square planar
$[Cu(NH_3)_4]^{2+}$	$dsp^2$	square planar
XeF <sub>4</sub>	$sp^3d^2$	square planar
BF <sub>4</sub>	$sp^3$	Tetrahedral
$[Ni(CN)_4]^{2-}$	$dsp^2$	square planar

14. (b, c)

(a, d)

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$
  
 $Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$ 

MnO<sub>2</sub> and PbO<sub>2</sub> are not peroxides but dioxides.

20. (a)

16. (a) 17. (c) 18. (c) 19. (b)

21. (a)

If bond order is +ve, the bond will be formed.

22.

Molecular orbital theory explains the magnetic nature of the molecules and ions.

23. B<sub>2</sub> KK  $\sigma(2s)^2$ ,  $\overset{*}{\sigma}(2s)^2$ ,  $\pi(2p_x)^1$ ,  $\pi(2p_y)^1$  $O_2 \ KK \ \sigma(2s)^2, \ {}^*\sigma(2s)^2, \ (\sigma(2p_x)^2, \ \pi(2p_x)^2, \ \pi(2p_x)^2, \ \pi(2p_x)^1, \ \pi(2p_x)^1$ Paramagnetic NO KK  $\sigma(2s)^2$ ,  $\mathring{\sigma}(2s)^2$ ,  $\sigma(2p_z)^2$ ,  $\pi(2p_x)^2$ ,  $\pi(2p_y)^2$ ,  $\mathring{\pi}(2p_x)^1$ 

Paramagnetic

(a-p), (b-p, q), (c-q, s), (d-r)

(a-q, s), (b-q, r, s), (c-q, r), (d-p, r)

# Practice Paper -2 . . . .

	PROPERTY OF STREET		
SECTION: 1			(b) property of catenation follows the order
			$C > Si > Ge = Sn > Pb$ $\Box$ (c) SiO <sub>2</sub> is linear and hybridisation of Si is $sp$
Straight Objective Type Questions			(d) solubility follows the order
This section contains 10 multiple choice questions. Each			BeSO <sub>4</sub> > MgSO <sub>4</sub> > CaSO <sub>4</sub> > SrSO <sub>4</sub> > BaSO <sub>4</sub>
	tion has 4 choices (a), (b), (c) and (d). Out of which only c	one	10. When KI (excess) is added to the following solutions
is co	prrect.		(i) CuSO <sub>4</sub> (ii) HgCl <sub>2</sub> (iii) Pb(NO <sub>3</sub> ) <sub>2</sub>
1.	Which species has the maximum number of lone pairs	of	separately:
	electrons on the central atom?		(a) a white precipitate of Cu <sub>2</sub> I <sub>2</sub> in I, an orange precipitate of
	(a) $ClO_3^-$		HgI <sub>2</sub> in II and a yellow precipitate in III
	(c) $I_3^-$		(b) a white precipitate of Cu <sub>2</sub> I <sub>2</sub> , HgI <sub>2</sub> and PbI <sub>2</sub> in each case
2.	The type of hybridisation in diborane is:		
	(a) $sp_2$		(c) a yellow precipitate in each case
_	(c) $sp^2$		(d) a white precipitate of Cu <sub>2</sub> I <sub>2</sub> in I, an orange precipitate
3.	For the redox reaction,		dissolving to HgI <sub>4</sub> <sup>2</sup> in II and a yellow precipitate of PbI <sub>2</sub>
	$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$		in III
	the correct coefficients for the balanced reaction are:	:	CECTION - 0
	$MnO_4^ C_2O_4^{2-}$ $H^+$		SECTION: 2
	(a) 2 5 16 (b) 16 5 2		Straight Multiple Choice Objective Type Questions
	(c) 5 16 2		This section contains 5 multiple choice questions. Each
	(d) 2 16 5		question has 4 choices. Out of which one or more than one may
4.	Among the following, hydration energy of Mg <sup>2+</sup> is great	ater	be correct.
	than that of:		Control Control
	(a) $Al^{3+}$		11. Which of the following pairs of elements have almost similar atomic radii?
	(c) Li <sup>+</sup>		(a) $Zr$ , $Hf$ $\Box$ (b) $Mo$ , $W$ $\Box$
5.	Reactions of HNO <sub>3</sub> (conc.) with I, S, P and C gi	ves	(a) $Z_{i,i}$ (b) $R_{i,j}$ (c) $C_{i,j}$ (d) $S_{i,j}$ $P_{b}$
	respectively:		12. $sp^3$ -hybridization is found in the structures of:
	(a) $HIO_3$ , $H_2SO_4$ , $H_3PO_4$ , $CO_2$		(a) O <sub>3</sub>
	(b) HIO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>3</sub> , CO <sub>2</sub>		(c) $NO_3^-$
	(c) I <sub>2</sub> O <sub>5</sub> , H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> , CO		13. The ONO bond angle is less than 180° in:
_	(d) I <sub>2</sub> O <sub>5</sub> , SO <sub>2</sub> , P <sub>2</sub> O <sub>5</sub> , CO <sub>2</sub>		(a) $NO_3^ \square$ (b) $NO_2^ \square$
0.	Which of the following is wrong?	_	(c) $NO_2$ $\square$ (d) $NO_2^+$ $\square$
	(a) Bond order of $O_2$ is greater than bond order of $O_2^-$		14. Which of the following function as catalysts for oxidation
	(b) Bond order of $O_2$ is less than bond order of $O_2^+$		of SO <sub>2</sub> to SO <sub>3</sub> in industrial process for production of H <sub>2</sub> SO <sub>4</sub> ?
	<ul> <li>(c) Bond order of N<sub>2</sub><sup>+</sup> is less than that of N<sub>2</sub></li> <li>(d) O<sub>2</sub><sup>2-</sup> is paramagnetic while O<sub>2</sub><sup>-</sup> is diamagnetic</li> </ul>		(a) $TiO_2$ $\Box$ (b) $PbO_2$ $\Box$
~		لسا	(c) Pt $\Box$ (d) $V_2O_5$
7.	(a) $XeO_3$ and $CaCO_3$ $\square$ (b) $XeO_2$ and $CaCN_2$		15. Which of the following reduction reactions are employed
	(c) $XeOF_3$ and $CaCN_2$ $\square$ (d) $XeOF_2$ and $CaCO_3$		practically in commercial extraction of metals?
			(a) $Fe_2O_3 + 2A1 \longrightarrow Al_2O_3 + 2Fe$
8.	$3\text{NaH}_2\text{PO}_4 \xrightarrow{230^{\circ}\text{C}} \text{Na}_3(\text{P}_3\text{O}_9) \xrightarrow{640^{\circ}\text{C}} (\text{NaPO}_3)_n$		(b) $\operatorname{Cr}_2\operatorname{O}_3 + 2\operatorname{Al} \longrightarrow \operatorname{Al}_2\operatorname{O}_3 + 2\operatorname{Cr}$
	<b>↓</b>		(c) $SnO_2 + 2C \longrightarrow Sn + 2CO$
	(D)		(d) $2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$
	Glassy solid The compound (D) is:		SECTION: 3
	(a) Bunsen's salt		Assertion-Reason Type Questions
	(c) Werner's salt		· · · · · · ·
9.	3	, [	Each question in this section contains Assertion (A) and
	(a) C can form $p\pi$ - $p\pi$ bonds with itself and with O or N	<b>ч</b> Ш	Reason (R). Each question has four choices, out of which only

Reason (R). Each question has four choices, out of which only one is correct. Mark your choice from the following options.

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is correct but (R) is false.
- (d) (A) is false but (R) is true.
- (A) Anhydrous magnesium chloride cannot be obtained by heating MgCl<sub>2</sub>·6H<sub>2</sub>O
  - (R) MgCl<sub>2</sub>·6H<sub>2</sub>O is highly stable and is unaffected by heat.
- 17. (A) Colour of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution depends on pH of the solution.
  - (R) In acidic medium, it has yellow colour and in basic medium, it has orange colour.
- 18. (A) The order of electron affinity of halogens is I > Br > Cl > F.
  - (R) Fluorine does not show variable oxidation states.
- **19.** (A) Alkali metals dissolve in liquid ammonia to give deep blue colour.
  - (R) Blue colour of the solution is due to the formation of ammoniated electron.
- 20. (A) Strength of various oxyacids follow the order

  HClO < HClO<sub>2</sub> < HClO<sub>3</sub> < HClO<sub>4</sub>
  - (R) Among the oxyacids of the same element, acidic nature increases with increase in the oxidation state of the element.

#### **SECTION: 4**

#### Linked Comprehension Type Questions .....

This section contains a paragraph. Based on this paragraph, multiple choice questions have been given. Each question has 4 choices. Out of which only one is correct.

Valence bond theory describes the bonding in complexes in terms of two electron coordinate covalent bonds resulting from the overlap of filled ligand orbitals with vacant metal hybrid orbitals that point in the direction of the ligands. This theory explains with reasonable success the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to provide a quantitative interpretation of

magnetic behaviour and explanation about optical properties of coordination compounds.

- 21. The correct order of magnetic moments (spin only value in BM) among the following is:
  - (a)  $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$
  - (b)  $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$
  - (c)  $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$
- (d)  $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$
- 22. The geometry of  $[Ni(CN)_4]^{2-}$  and  $[NiCl_4]^{2-}$  are:
  - (a) both square planar
  - (b) both tetrahedral □
    (c) tetrahedral and square planar respectively □
  - (d) square planar and tetrahedral respectively
- 23.  $[Fe(H_2O)_6]^{2+}$  and  $[Fe(CN)_6]^{4-}$  differ in:
  - (a) geometry, magnetic moment ☐
    (b) magnetic moment, colour ☐
  - (c) geometry, hybridisation
  - (d) hybridisation, number of unpaired electrons

## **SECTION: 5**

## Matrix-Match Type Questions .....

Each question contains statements given in two columns, which have to be matched.

24. Match List-I with List-II:

#### List-I

## List-II

- (a) Linear shape
- (p) CO<sub>2</sub>
- (b) sp-hybridisation
- (q)  $I_3^-$
- (c)  $sp^3d$ -hybridisation
- (r) C<sub>2</sub>H<sub>2</sub>
- (d) CS<sub>2</sub> is isostructural to
- (s) NCO
- 25. Match Column-II with Column-II:

#### Column-I

## Column-II

- (a) Ammonium nitrate
- (p) Fertilizer
- (b) Sodium thiosulphate
- (q) Purgative
- (c) Mercurous chloride
- (r) Antichlor
- (d) Silver bromide
- (s) Photography

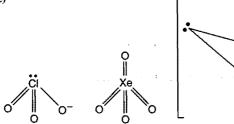
(e) Amatol

(t) Explosive

## Solwelon

## Practice Paper: 2 ....

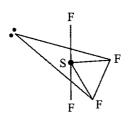
1. (c)



One lone pair

No lone pair

Three lone pairs



One lone pair

2. (b)

3. (a)

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O_3$$

4. (d)

The degree of hydration depends on the size of the ion. The size of Mg<sup>2+</sup> ion is less than Na<sup>+</sup> ion and more than Be<sup>2+</sup>, Al<sup>3+</sup> and Li<sup>+</sup> ions. Hence, Hydration energy of Mg<sup>2+</sup> ion is greater than that of Na<sup>+</sup> ion.

5. (a)

$$\begin{split} I_2 + 10 \text{HNO}_3 &\longrightarrow 2 \text{HIO}_3 + 10 \text{NO}_2 + 4 \text{H}_2 \text{O} \\ \text{S} + 6 \text{HNO}_3 &\longrightarrow \text{H}_2 \text{SO}_4 + 6 \text{NO}_2 + 2 \text{H}_2 \text{O} \\ \text{P} + 10 \text{HNO}_3 &\longrightarrow 2 \text{H}_3 \text{PO}_4 + 10 \text{NO}_2 + 2 \text{H}_2 \text{O} \\ \text{C} + 4 \text{HNO}_3 &\longrightarrow \text{CO}_2 + 4 \text{NO}_2 + 2 \text{H}_2 \text{O} \end{split}$$

6. (d)

Bond order of 
$$O_2 = 2$$
,  $O_2^+ = 2.5$ ,  $O_2^- = 1.5$ ,  $N_2 = 3$ ,  $N_2^+ = 2.5$   
 $O_2^{2-} =$  no unpaired electrons, hence diamagnetic  
 $O_2^- =$  one unpaired electron, hence paramagnetic

7. (a)

$$2XeF_4 + 3H_2O \longrightarrow Xe + XeO_3 + F_2 + 6HF$$
  
 $CaCN_2 + 5H_2O \longrightarrow CaCO_3 + 2NH_4OH$ 

8. (b)

(D) is sodium hexametaphosphate, (NaPO<sub>3</sub>)<sub>6</sub>, which is called Graham's salt.

9. (c)

 $SiO_2$  is three dimensional giant. Silicon undergoes  $sp^3$  hybridisation.

10. (d)

$$\begin{split} 2\text{CuSO}_4 + 4\text{KI} & \longrightarrow \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2 \\ & \text{White} \\ \text{HgI}_2 + 2\text{KI} & \longrightarrow \text{K}_2\text{HgI}_4 \\ \text{Pb(NO}_3)_2 + 2\text{KI} & \longrightarrow \text{PbI}_2 + 2\text{KNO}_3 \\ & \text{Yellow} \end{split}$$

11. (a, b, c)

Due to lanthanide contraction, the atomic radii of Zr and Hf, Mo and W are almost similar. In case of Co and Ni, increase in nuclear charge is almost balanced by shielding effect and as a result, both have nearly the same atomic radii.

12. (b, d)

NH<sub>3</sub> and H<sub>2</sub>O contain sp<sup>3</sup>-hybridised N and O atoms respectively.

13. (a, b, c)

 $NO_3^-$  has  $sp^2$  hybridisation. The bond angle is 120°.

 $NO_2$  and  $NO_2^-$  have  $sp^2$  hybridisation. Due to presence of one electron pair on  $NO_2^-$ , the repulsion on the bond pairs is more and thus, the angle is less, *i.e.*, 115° while in  $NO_2$ , one unshared electron is present on N-atom, the bond angle is more, *i.e.*, 132°.

NO<sub>2</sub><sup>+</sup> has sp-hybridisation, hence bond angle is 180°.

14. (c, d)

In contact process, either platinum or V<sub>2</sub>O<sub>5</sub> can be used as catalysts.

15. (b, c, d)

16. (c)

MgCl<sub>2</sub>·6H<sub>2</sub>O undergoes hydrolysis on heating.

$$MgCl_2 \cdot 6H_2O \longrightarrow Mg(OH)Cl + HCl + 5H_2O$$

17. (c)

In the solution, the following equilibria exists.

$$Cr_2O_7^{2-} + H_2O \Longrightarrow 2CrO_4^{2-} + 2H^+$$

In acidic medium,  $Cr_2Q_7^2$  ions exist which have orange colour while in basic medium,  $CrQ_4^2$  ions exist which have yellow colour.

18. (ď

The order of electron affinity is

Fluorine being the most electronegative always shows -1 oxidation state only.

19. (a)

Alkali metal atoms lose electrons which combine with ammonia molecules

$$M + (x + y)NH_3 \longrightarrow [M(NH_3)_x]^+ + e(NH_3)_y$$
Solvated

Solvated electron is responsible for blue colour.

20. (a)

21. (d)

[MnCl<sub>4</sub>]<sup>2-</sup> has tetrahedral geometry, *i.e.*, 5 unpaired electrons are present.

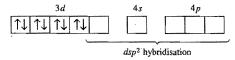
$$Mn^{2+}$$
  $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$   $\downarrow g$   $\downarrow g$  hybridisation

 $[Fe(CN)_6]^{4-}$  has octahedral geometry, i.e., it has no unpaired electron.

[CoCl<sub>4</sub>]<sup>2-</sup> has tetrahedral geometry, i.e., it has 3 unpaired electrons.

22. (d)

CN<sup>-</sup> is a strong ligand. Electrons in rearranged in 3d-orbitals of Ni<sup>2+</sup> ion. It undergoes  $dsp^2$  hybridisation in forming [Ni(CN)<sub>4</sub>]<sup>2-</sup> complex.



Cl<sup>-</sup> is a weak ligand. Electrons are not rearranged in 3d-orbitals of Ni<sup>2+</sup> ion. It undergoes  $sp^3$  hybridisation in forming [NiCl<sub>4</sub>]<sup>2-</sup> complex.

23. (b)

 $[Fe(H_2O)_6]^{2+}$  is paramagnetic while  $[Fe(CN)_6]^{4-}$  is diamagnetic.  $[Fe(H_2O)_6]^{2+}$  has pale green colour while  $[Fe(CN)_6]^{4-}$  has yellow colour

**24.** (a-p, q, r, s); (b-p, r, s); (c-q); (d-p)

25. (a-p, t); (b-r, s); (c-q); (d-s); (e-t)

# Practice Paper —3 ....

## **SECTION: 1**

## Straight Objective Type Questions .....

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d). Out of which only one is correct.

1.

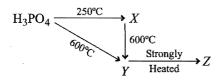
atom is:

(a)  $[Co(NH_3)_6]^{3+}$ 

(c)  $[Cr(H_2O)_6]^{3\nu}$ 

(a)  $Al^{3+} + 3Cl^{-}$ 

When dissolved in water, it gives:



	X, $Y$ and $Z$ are :				
	•				
	(a) $H_4P_2O_7$ , $HPO_3$ and $P_4O_{10}$ respectively	느			
	(b) HPO <sub>3</sub> , H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> and P <sub>4</sub> O <sub>10</sub> respectively				
	(c) H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> , H <sub>3</sub> PO <sub>3</sub> and P <sub>4</sub> O <sub>6</sub> respectively				
	(d) H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> , HPO <sub>3</sub> and P <sub>4</sub> O <sub>6</sub> respectively				
2.	The types of bonds present in CuSO <sub>4</sub> ·5H <sub>2</sub> O are:				
	(a) electrovalent and covalent				
	(b) electrovalent and coordinate covalent				
	(c) electrovalent, covalent, coordinate and hydrogen bonds				
	(d) covalent and coordinate covalent				
3.	For $A + KOH + Air \xrightarrow{Heat} B$				
	$B + O_3 + H_2O \longrightarrow C$ (Pink)				
	Which of the following is correct?				
	(a) A is black (MnO <sub>2</sub> ), B is blue ( $K_2MnO_4$ ) and C is	pink			
	(KMnO <sub>4</sub> )				
	(b) A is black (MnO <sub>2</sub> ), B is green (K <sub>2</sub> MnO <sub>4</sub> ) and C is	pink			
	(KMnO <sub>4</sub> )				
	(c) A is colourless (MnO <sub>2</sub> ), B is blue ( $K_2MnO_4$ ) and C is	pink			
	(KMnO <sub>4</sub> )				
	(d) A is green (MnO <sub>2</sub> ), B is green (K <sub>2</sub> MnO <sub>4</sub> ) and C is	pink			
	(KMnO <sub>4</sub> )				
4.	The complex ion which has no d-electrons in the central n	netal			

 $\Box$  (b)  $[Fe(CN)_6]^{3-}$ 

 $\Box$  (b)  $[Al(H_2O)_6]^{3+} + 3Cl^{-}$ 

☐ (d) [MnO<sub>4</sub>]

5. Aluminium chloride exists as dimer, Al<sub>2</sub>Cl<sub>6</sub> in solid state as well as in solution of non-polar solvents such as benzene.

(c)  $[Al(OH)_6]^{3-} + 3HCl \square$  (d)  $Al_2O_3 + 6HCl$ 

are correct?

	(a) Fe(CO) <sub>5</sub>	L	(b) [FeCl <sub>4</sub> ]	L
	(c) $Fe_4[Fe(CN)_6]_3$		(d) $[Fe(H_2O)_5NO]^{2+}$	
7.	Consider the following	ng compl	ex	
	[Co(NH <sub>3</sub> ) <sub>5</sub> CO <sub>3</sub> ]ClO <sub>4</sub>			٠
	The coordination number, oxidation number, number of			her of
		•	paired $d$ -electrons on the	
	are respectively:	oci oi un	paried a-electrons on the	. metai
	(a) 6, 3, 6, 0	П	(b) 7, 2, 7, 1	П
	(c) 7, 1, 6, 4	$\overline{\Box}$	(d) 6, 2, 7, 3	Ä
				-
8.	$(KCl + K_2Cr_2O_7 + H$	$l_2SO_4)-$	————Red gas	
	$(B) \leftarrow \frac{\text{CH}_3\text{COOH}}{(\text{CH}_3\text{COO})_2\text{Pb}}$	$-(A) \leftarrow$	Dil. NaOH	
	(CH <sub>3</sub> COO) <sub>2</sub> Pb	` .	*	
	The formulae of (A)	and (B)	with colours are:	
	(a) Na <sub>2</sub> CrO <sub>4</sub> , yellow			
	(b) Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , orang			
	(c) Cr(OH) <sub>3</sub> , green a	nd (CH <sub>3</sub> 0	COO) <sub>3</sub> Cr, green	
	(d) CrO <sub>2</sub> Cl <sub>2</sub> , red and	(CH <sub>3</sub> CC	OO) <sub>3</sub> Cr, green	
9.	Among the following	g molecu	iles:	
•.	(i) XeO <sub>3</sub> (ii) XeOF <sub>2</sub>	(iii) X	eF <sub>6</sub>	
	Those having same	number (	of lone pairs on Xe are:	
	(a) (i) and (ii) only		(b) (i) and (iii) only	
	(c) (ii) and (iii) only		(d) (i), (ii) and (iii)	
10.	A gas 'X' is passe	ed throug	gh water to form a sa	turated
	solution. The aqueous solution on treatment with silver			silver
	nitrate gives a white precipitate. The saturated aqueous			
	solution also dissolves magnesium ribbon with evolution of			
	colourless gas 'Y'. '	X' and '	Y' are:	
	(a) $X = CO_2$ ; $Y = Cl_2$	2 🗆	(b) $X = Cl_2$ ; $Y = CO_2$	
			(d) $X = H_2$ ; $Y = Cl_2$	
			, ,	
	SI	CTIC	N : 2	•
	<u>VI</u>		/14 - 4-	
C/m	aiaht Multinla Ch	oice O	bjective Type Quest	ione
MEN (	uigiii muuipie Cii	vice O	ojecuve rype Quesu	wiis
7	This section contain.	s 5 mui	ltiple choice questions	. Each
question has 4 choices. Out of which one or more than one may				
be i	correct.			
11.	Which of the follow	ving have	e planar structure?	
	(a) $I_3^-$		(b) H <sub>2</sub> O <sub>2</sub>	
	(c) $B_2H_6$		(d) $[Ni(CN)_4]^{2-}$	$\overline{\Box}$
12.	Three centre-two el	ectron bo		
444 4	(a) $B_2H_6$		(b) Al <sub>2</sub> (CH <sub>3</sub> ) <sub>6</sub>	П
	(a) B <sub>2</sub> H <sub>6</sub> (c) BeH <sub>2</sub>		(d) BeCl <sub>2</sub>	
12	- · · · · · · · · · · · · ·		_ · · ·	un atala
13.	MINCH OF THE TOHOW	mg staten	nents about alkaline earth	imerars

6. Iron exhibits the +1 oxidation state in:

	<ul> <li>(a) Hydration energy of Sr<sup>2+</sup> is greater than that of Be<sup>2+</sup>□</li> <li>(b) CaCO<sub>3</sub> decomposes at a higher temperature than BaCO<sub>3</sub></li> </ul>	SEC	TION: 4	
	(c) Ba(OH) <sub>2</sub> is stronger base than Mg(OH) <sub>2</sub>	Linked Comprehension Type Questions  This section contains a paragraph. Based on the paragraph, multiple choice questions have been given. Each question has 4 choices, out of which only one is correct.  When the halogen atom combines with an element of lesser electronegativity, it shows -1 oxidation state. On the other hand, when it combines with an element having higher electronegativity it exhibits +1 oxidation state. Chlorine and higher halogens show positive oxidation states as the electrons in the valency shell can be promoted to vacant d-orbitals. These elements can show +3.		
	SECTION: 3	_	show positive oxidation state?	_
Ass	sertion-Reason Type Questions	<ul><li>(a) Chlorine</li><li>(c) Bromine</li><li>22. In which of the following</li></ul>	☐ (b) Fluorine ☐ (d) Iodine ng, iodine has the highest oxide	□ □ ation
one (	<ul> <li>is correct. Mark your choice from the following options.</li> <li>a) Both (A) and (R) are true and (R) is the correct explanation of (A).</li> <li>b) Both (A) and (R) are true but (R) is not the correct explanation of (A).</li> <li>c) (A) is correct but (R) is false.</li> </ul>	excited state of central  (a) square pyramidal  (c) distorted octahedra	☐ (b) T-shape  I ☐ (d) octahedral	cond
	(d) (A) is false but (R) is true.	SEC	TION: 5	
17.	<ul> <li>(A) LiCl is more ionic than NaCl.</li> <li>(R) Smaller the size of cation, greater is the polarising power.</li> <li>(A) Among chalcogens, tendency of catenation is maximum for sulphur.</li> <li>(R) S—S bond dissociation energy is higher than O—O bond dissociation energy.</li> <li>(A) Bond order of N<sub>2</sub><sup>+</sup> and N<sub>2</sub><sup>-</sup> are same.</li> <li>(R) N<sub>2</sub><sup>+</sup> is more stable than N<sub>2</sub><sup>-</sup>.</li> </ul>	This section contains two	estions  o questions. Each question con umns, which have to be matched olumn-II:  Column-II  (Precipitating agent)	tains
19.	(A) $[Cu(NH_3)_4]^{2+}$ is coloured, while $[Cu(CN)_4]^{3-}$ ion is	(a) Pb <sup>2+</sup>	(p) Dilute HCl	
	colourless.	(b) $Hg_2^{2+}$	(q) H <sub>2</sub> S in presence of HC	1
20.	<ul> <li>(R) [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> has dsp<sup>2</sup> hybridisation.</li> <li>(A) Superoxides of alkali metals are paramagnetic.</li> </ul>	(c) Sn <sup>2+</sup>	(r) Sulphide soluble in yel ammonium sulphide	llow
	(R) Superoxides contain the ion which has one unpaired electron.	(d) $Hg^{2+}$	(s) Sulphide insoluble in yo ammonium sulphide	ellov
		25. Match Column-I with C		
		Column-I	Column -II	
		<ul><li>(a) Linear shape</li><li>(b) sp-hybridisation</li></ul>	(p) CO <sub>2</sub>	
		(c) $sp$ -nyoridisation (c) $sp^3d$ -hybridisation	(q) XeF <sub>2</sub>	
		CALAD A-HVDEROSHIAN		

(d)  $CS_2$  is isostructural to

(s)  $I_3^-$ 

# Solution

#### Practice Paper: 3....

1. (a) 
$$2H_{3}PO_{4} \xrightarrow{250^{\circ}C} H_{4}P_{2}O_{7} + H_{2}O$$

$$(X)$$

$$H_{3}PO_{4} \xrightarrow{600^{\circ}C} HPO_{3} + H_{2}O$$

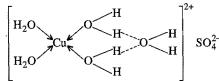
$$(Y)$$

$$H_{4}P_{2}O_{7} \xrightarrow{600^{\circ}C} 2HPO_{3} + H_{2}O$$

$$(Y)$$

$$4HPO_{3} \xrightarrow{Strongly} P_{4}O_{10} + 2H_{2}O$$

2. (c) CuSO<sub>4</sub>·5H<sub>2</sub>O can be represented as :



3. (b) 
$$2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \longrightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$$

$$(A) \qquad (air) \qquad (B) \qquad Green$$
 $2\text{K}_2\text{MnO}_4 + \text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{KMnO}_4 + 2\text{KOH} + \text{O}_2$ 

$$(C) \qquad Pink$$

- **4.** (d) In  $[MnO_4]^-$ ,  $Mn^{7+}$  ion has the configuration [Ar]  $3d^04s^0$ , *i.e.*, all the 3d electrons and 4s electrons have been lost.
- 5. **(b)**  $Al_2Cl_6 + 12H_2O \rightleftharpoons 2[Al(H_2O)_6]^{3+} + 6Cl^{-1}$
- 6. (d)

#### Oxidation number

 $\begin{aligned} &\text{Fe(CO)}_5 & & 0 \\ &[\text{FeCl}_4]^\top & +3 \\ &\text{Fe}_4[\text{Fe(CN)}_6]_3 & +3, +2 \text{ respectively} \\ &[\text{Fe(H}_2\text{O)}_5\text{NO}]^{2+} & +1 \end{aligned}$ 

 $x + 5 \times 0 + 1 = +2$  or x = +1

- 7. (a)
  - Coordination number

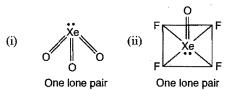
Oxidation number 3  $\frac{3d}{3} + \frac{4s}{3} + \frac{4s}{3}$ 

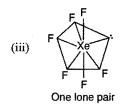
No. of *d*-electrons 6 No. of unpaired electrons 0

8. (a)

6

9. (d)





10. (c)  $\begin{array}{c} \operatorname{Cl}_2 + \operatorname{H}_2\operatorname{O} \longrightarrow \operatorname{HCl} + \operatorname{HClO} \\ (X) \\ \operatorname{HCl} + \operatorname{AgNO}_3 \longrightarrow \operatorname{AgCl} + \operatorname{HNO}_3 \\ \operatorname{White ppt.} \\ \operatorname{2HCl} + \operatorname{Mg} \longrightarrow \operatorname{MgCl}_2 + \operatorname{H}_2 \\ (Y) \end{array}$ 

11. (a, d)  $I_3$ —Linear;  $[Ni(CN)_4]^2$ —square planar

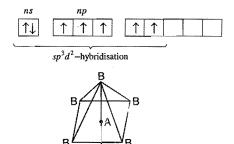
- 12. (a, b)
- 13. (c, d)
- 14. (a, b, c) CO<sub>2</sub> and SO<sub>2</sub> turn lime water milky.
- 15. (a, b, c)
- 16. (d) LiCl is less ionic than NaCl as Li<sup>+</sup> ion is smaller than Na<sup>+</sup> ion. Hence, it has more polarising power than Na<sup>+</sup> ion.
- 17. (a)
- 18. (b) Both statements are correct.

$$N_2^+$$
, B.O. =  $\frac{9-4}{2}$  = 2.5  
 $N_2^-$ , B.O. =  $\frac{10-5}{2}$  = 2.5

 $N_2^+$  is more stable than  $N_2^-$  as it contains less number of antibonding electrons.

- 19. (b) Both the statements are correct.
- 20. (a) Presence of unpaired electron in superoxides of alkali metals make them paramagnetic.
- (b) Fluorine being highest electronegative element shows only -1 oxidation state.
- 22. (c)  $HIO_4$ , +1+x-8=0or x=+7
- 23. (a)

Second excited state



- **24.** (a-p, q, s); (b-p); (c-q, r); (d-q, s)
- 25. (a-p, q, r, s); (b-p, r); (c-q, s); (d-p)

# Practice Paper —4 . . . .

SECTION: 1 Storage	7. Which of the following reactions is not taking place the extraction of Ag from Ag <sub>2</sub> S by cyanide process	_
his section contains 9 multiple choice questions. Each tion has 4 choices (a), (b), (c) and (d). Out of which only one	(a) $Ag_2S + CN^- \longrightarrow [Ag(CN)_2]^- + S^2^-$ (b) $Zn + [Ag(CN)_2]^- \longrightarrow [Zn(CN)_4]^{2^-} + Ag$ (c) $Cu + [Ag(CN)_2]^- \longrightarrow [Cu(CN)_4]^{2^-} + Ag$ (d) $S^{2^-} \longrightarrow SO_4^{2^-} + S + S_2O_3^{2^-}$	_ _ _
An inorganic compound liberates oxygen when heated, turns an acid solution of KI brown and decolourises acidified KMnO <sub>4</sub> solution. The substance is:  (a) $H_2O_2$	<ul> <li>(a) pentamminechloridocobalt (III) ion</li> <li>(b) triamminetrichloridocobalt (III)</li> <li>(c) dichlorido bis (ethylenediamine) cobalt (III) ion</li> <li>(d) tetraamminedichloridocobalt (III) ion</li> </ul>	
Na + NH <sub>3</sub> $\longrightarrow$ (A) $\longrightarrow$ (B) $\longrightarrow$ gas (X)  (a) (A) On reaction with water gives NaOH and N <sub>2</sub>		
(b) (B) Contains anion of linear geometry $\Box$ (c) (X) is coloured $\Box$	SECTION: 2	
	This section contains 4 multiple choice questions	. Each
option: A. Boron fibres (i) Heat resistant glass	most abundant non-metal  (b) Iron is the most abundant transition metal  (c) Iodine is found in sea cucumber  (d) Vanadium is found in sea weeds  11. Oleum which is labelled as "109% pure H <sub>2</sub> SO <sub>4</sub> " sug	
B. Borax  (ii) Bullet proof vest  C. Aluminium  (iii) Filler in automobile tyre  D. Carbon black  (iv) Transport industry  (a) A-(i), B-(ii), C-(iii), D-(iv)  (b) A-(ii), B-(i), C-(iv), D-(iii)  (c) A-(ii), B-(iii), C-(i), D-(iv)  (d) A-(iii), B-(ii), C-(i), D-(iv)  Number of oxygen atoms shared per SiO <sub>4</sub> <sup>4</sup> tetrahedron in;  (i) two dimensional sheet structured silicates  (ii) cyclic silicates and  (iii) single strand chain silicates are, respectively:	<ul> <li>(b) Copper sulphate solution reacts with K<sub>4</sub>Fe(CN)<sub>6</sub></li> <li>(c) Ferric chloride reacts with K<sub>4</sub>Fe(CN)<sub>6</sub></li> <li>(d) Anhydrous white CuSO<sub>4</sub> is dissolved in water</li> </ul>	5 O
	his section contains 9 multiple choice questions. Each tion has 4 choices (a), (b), (c) and (d). Out of which only one orrect.  An inorganic compound liberates oxygen when heated, turns an acid solution of KI brown and decolourises acidified KMnO4 solution. The substance is:  (a) H2O2	sight Objective Type Questions

$$K_{2}MnO_{4} \xrightarrow{H_{2}SO_{4}} KMnO_{4}$$

$$(B)$$
Purple
$$2KMnO_{4} + H_{2}SO_{4} \longrightarrow Mn_{2}O_{7} + H_{2}O + K_{2}SO_{4}$$

$$(conc.) \qquad (C)$$

$$2Mn_{2}O_{7} \longrightarrow 4MnO_{2} + 3O_{2}$$

$$(D)$$

The cation in (D) is  $M^{4+}$ . E.C. of  $M^{4+} = [Ar]3d^3$ 

Thus, number of unpaired electrons in  $M^{4+} = 3$ .

16. (1) 
$$Xe + 3F_2 \xrightarrow{\text{High Press.}} XeF_6$$
  
 $1:20 \xrightarrow{\text{Ni-tube}} XeO_3 + 6HF$   
 $(X)$ 

	58	5 <i>p</i>	·	5 <i>d</i>	
E.C. of Xe in ground state	ŤΨ	11 11 11	,		
E.C. of Xe in excited state	11	$\uparrow$ $\uparrow$ $\uparrow$	1 1	1	
	$sp^3$ hyb.				

In XeO<sub>3</sub>, Xenon undergoes sp<sup>3</sup> hybridisation giving tetrahedral configuration. There are three sigma bonds with three hybrid orbitals and three  $\pi$ -bonds along with one lone pair of electrons.



17. (4) 
$$MCl_x + xAgNO_3 \longrightarrow xAgCl + M(NO_3)_x$$

Number of moles of AgNO3 used for 0.1 mole of MCl<sub>x</sub>  $=\frac{500}{1000} \times 0.8 = 0.4 \text{ mol.}$ 

Thus, 1 mole of MClx requires 4 moles of AgNO<sub>3</sub>

Calcium carbide on hydrolysis gives acetylene.

#### 19. (a)

**(b)** 20.

#### 21. (c)

NaCl and CaCl2 are added to make the fused mass as good conductor and also to lower the fusion temperature of anhydrous MgCl<sub>2</sub>.

**22.** 
$$(a-q, s), (b-r), (c-q, s), (d-p, s)$$

#### 25. (c)

#### 26. (a)

On heating polyhalide, the smallest halogen remains attached with the metal because this forms a salt with higher lattice energy.

#### 27. (c)

Iodine undergoes  $sp^3d^2$  hybridization giving octahedral configuration having three hybrid orbitals with single electron each, one vacant hybrid orbital and two hybrid orbitals have paired electrons each. The ion consists three covalent bonds, one coordinate bond and two lone pairs.



Yb: 70 [Xe] 
$$4f^{14}$$
,  $6s^2$   
Lu: 71 [Xe]  $4f^{14}$ ,  $5d^1$ ,  $6s^2$ 

Lu: 71 [Xe] 
$$4f^{14}$$
,  $5d^1$ ,  $6s^2$ 

#### 30. (d)

Lu3+ is the smallest in size.

# Practice Paper —5 ...

SECTION: 1		(b) two unpaired electrons and is diamagnetic ☐ (c) one unpaired electron and is paramagnetic ☐		
Stre	aight Objective Type Questions	(d) no unpaired electron and is diamagnetic.		
	his section contains 9 multiple choice questions. Each	SECTION: 2		
ques	stion has 4 choices (a), (b), (c) and (d). Out of which only one			
is co	orrect.	Straight Multiple Choice Objective Type Questions		
1.	HNO <sub>3</sub> acid solutions A and B have concentrations 0.5 N and			
	0.1 N respectively. The volume of solutions A and B required	This section contains 4 multiple choice questions. Each		
	to make 2 L of 0.2 N HNO <sub>3</sub> acid solution is:	question has 4 choices. Out of which one or more than one may		
	(a) $0.5 \text{ L of } A \text{ and } 1.5 \text{ L of } B$	be correct.		
	(b) 1.5 L of A and 0.5 L of B	10. Which of the following are correct statements?		
	(c) 1.0 L of A and 1.0 L of B	(a) Solid PCl <sub>5</sub> exists as [PCl <sub>4</sub> ] <sup>+</sup> [PCl <sub>6</sub> ] <sup>-</sup>		
	(d) 0.75 L of A and 1.25 L of B	(b) Solid PBr <sub>5</sub> exists as [PBr <sub>4</sub> ] <sup>+</sup> Br \qquad \qquad		
2.	The purity of H <sub>2</sub> O <sub>2</sub> in a given sample is 85%. The weight of	(c) Solid N <sub>2</sub> O <sub>5</sub> exists as [NO <sub>2</sub> ] <sup>+</sup> [NO <sub>3</sub> ] <sup>-</sup>		
	impure sample of H <sub>2</sub> O <sub>2</sub> which requires 10 mL of 1N KMnO <sub>4</sub>	(d) Oxides of phosphorus P <sub>2</sub> O <sub>3</sub> and P <sub>2</sub> O <sub>5</sub> exist as monomers		
	in a titration in acidic medium is:			
	(a) $2g$ $\square$ (b) $0.2g$ $\square$	11. Which of the following isomerisms are shown by the complex		
	(c) $0.17  \mathrm{g}$	[CoCl <sub>2</sub> (OH) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Br?		
3.	TlI <sub>3</sub> is an ionic compound which furnishes the following ions:	(a) Ionisation		
	(a) $TI^{3+}$ and $I_3^ \Box$ (b) $TI^{3+}$ and $I^ \Box$	(c) Geometrical		
	(c) $Tl^+$ and $I^ \Box$ (d) $Tl^+$ and $I_3^ \Box$	12. CS <sub>2</sub> is isostructural with :		
4.	$Be_2C + 4H_2O \longrightarrow 2X + CH_4$	(a) BeCl <sub>2</sub>		
	$X + 2$ NaOH $\longrightarrow Y + 2$ H <sub>2</sub> O	(a) $C_2H_2$ $\Box$ (b) $C_2H_2$ $\Box$ (c) $C_2H_2$ $\Box$ (d) $C_2H_2$ $\Box$		
	X and Y formed in the above two reactions are:	13. Which of the following represents the same element?		
	(a) BeCO <sub>3</sub> and Be(OH) <sub>2</sub> respectively $\Box$	(a) 106		
	(b) Be(OH) <sub>2</sub> and Na <sub>2</sub> BeO <sub>2</sub> respectively	(c) Ha		
	(c) $[Be(OH)_4]^{2-}$ and $Be(OH)_2$ respectively	(c) Im — — (d) of (sourcestum) —		
	(d) BeO and Be(OH) <sub>2</sub> respectively $\Box$			
5.	Which of the following species represents the example of	SECTION: 3		
	dsp <sup>2</sup> hybridization?			
:	(a) $[Fe(CN)_6]^3$	Integer Answer Type Questions		
	(c) $[Ag(CN)_2]^{-}$ $\Box$ (d) $[Co(CN)_6]^{3-}$ $\Box$			
6.	The fluoride of xenon with zero dipole moment is:	This section contains 4 questions. The answer to each of the		
	(a) $XeF_6$	questions is a single-digit integer ranging from 0 to 9.		
_	(c) $XeF_4$	14. An acid is formed by heating orthophosphoric acid at		
7.	A greenish yellow gas reacts with an alkali metal hydroxide	250-260°C. The number of series of salts formed by this acid		
	to form a halate which can be used in fireworks and safety	are:		
	matches. The gas and halate respectively are:	15. How many moles of carbon monoxide are obtained when		
	(a) $Cl_2$ , $KClO_3$	one mole of potassium ferrocyanide is heated with conc.		
_	(c) I <sub>2</sub> , KIO <sub>3</sub>	sulphuric acid?		
8.	In BF <sub>3</sub> , the B-F bond length is 1.30Å. When BF <sub>3</sub> is allowed	16. The ratio of lone pairs and the number of S-S bonds in S <sub>8</sub>		
•	to be treated with Me <sub>3</sub> N, it forms an adduct, Me <sub>3</sub> N $\rightarrow$ BF <sub>3</sub> ,	molecule is:		
	the bond length of B-F in the adduct is:	17. For the reaction,		
	(a) greater than 1.30 Å	$M^{x+} + \text{MnO}_{4}^{-} \longrightarrow MO_{3}^{-} + \text{Mn}^{2+} + 1/2 O_{2}$		
•	(c) equal to 1.30 Å	If one mole of $MnO_4^-$ oxidises 1.67 moles of $M^{x+}$ to $MO_3^-$ ,		
У.	Dinitrogen tetroxide (N <sub>2</sub> O <sub>4</sub> ) has:	then the value of $x$ in the reaction would be:		
	(a) two unpaired electrons and is paramagnetic			

#### **SECTION: 4**

#### Assertion-Reason Type Questions .....

Each question in this section contains Assertion (A) and Reason (R). Each question has four choices, out of which only one is correct. Mark your choice from the following options.

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is true but (R) is false.
- (d) (A) is false but (R) is true.
- 18. (A) CO and  $O_2$  both combine with haemoglobin.
  - (R) CO has greater affinity for haemoglobin than O<sub>2</sub>.
- 19. (A) Normal hydrogen consists of a mixture of two forms, ortho (75%) and para (25%).
  - (R) Pure ortho form can be obtained at low temperature but pure para form can not be obtained.
- 20. (A) KCN gives K<sub>3</sub>Cu (CN)<sub>4</sub> complex compound with CuSO<sub>4</sub> solution.
  - (R) KCN reduces Cu<sup>2+</sup> to Cu<sup>+</sup> and then forms a complex compound.
- 21. (A) The first ionisation energy of Be is greater than that of B.
  - (R) 2p-orbital is lower in energy than 2s-orbital.

#### **SECTION: 5**

#### Matrix-Match Type Questions .....

This section contains 3 questions. Each question contains statements given in two columns, which have to be matched.

22. Match Column-I with Column-II.

## Column-I

#### Column-II

- (a) K<sub>4</sub>Fe(CN)<sub>6</sub>
- (p) Geometrical isomers
- (b)  $[Pt(NH_3)_4Cl_2]Br_2$
- (q) Paramagnetic
- (c)  $[Co(NH_3)_3Cl_3]$
- (r) Diamagnetic
- (d)  $[NiCl_4]^{2}$
- (s) Metal ion with +2 oxidation state
- 23. Match Column-I with Column-II.

#### Column-I

#### Column-II

(a) Brass

- (p) Copper
- (b) Bronze
- (q) Zinc
- (c) German silver
- (r) Nickel
- (d) Constantan
- (s) Tin
- 24. Match Column-I with Column-II.

#### Column-I

#### Column-II

- (a)  $4s^2 4p^6$
- (p) Metal
- (b)  $6s^1 4f^{14} 5d^{10}$
- (q) Non-metal

(c)  $4f^1 5s^2 5p^6 5d^1 6s^2$ (d)  $4s^2 3d^{10} 4p^5$ 

在一時間的事物也們將經過學在一個

- (r) Noble gas
- (s) Lanthanide

 $\Box$ 

#### **SECTION: 6**

#### Linked Comprehension Type Questions .....

This section contains 2 paragraphs. Based on each paragraphs, 3 multiple choice questions have to be answered. Each question has four choices, out of which only one is correct.

#### Comprehension: 1

Xenon having nearly the same ionisation energy as oxygen forms a large number of compounds like xenon fluorides, oxyfluorides, oxides and perxenates. Xenon exhibits various oxidation states from +2 to +8. Perxenates are powerful oxidants and  $XeO_3$  is a powerful explosive.

- **25.** The hybridization of Xe in XeO<sub>2</sub>F<sub>2</sub> and its shape are : (a)  $sp^3d^2$ , T-shaped  $\Box$  (b)  $sp^3d$ , see-saw  $\Box$ 
  - (c)  $sp^3$ , tetrahedral  $\Box$  (d)  $sp^3d$ , V-shape
- **26.** The number of lone pairs of electrons in XeF<sub>2</sub>, XeF<sub>4</sub>, XeF<sub>6</sub> and XeOF<sub>2</sub> are respectively:
- 27. The wrong statement is:
  - (a) Perxenates are  $[XeO_6]^{4-}$
  - (b) Perxenates are coloured and strong reductants
  - (c) Oxidation number of Xe in perxenates is + 8
  - (d) Perxenates are formed by hydrolysis of xenon hexafluoride with strong alkalies.

#### Comprehension: 2

Metal nitrate (A) on heating decomposes, leaving a solid residue (B) which goes into solution with dilute HCl. The solution of (B) gives a white precipitate with ammonium carbonate solution. The precipitate is dissolved in dilute HCl and the solution is treated with K<sub>2</sub>CrO<sub>4</sub> solution to give a yellow precipitate (C). The solution (B) reacts with dil. H<sub>2</sub>SO<sub>4</sub> also gives a white precipitate (D), insoluble in dilute HCl and HNO<sub>3</sub>. The precipitate (D) is a part of a white pigment lithopone.

- 28. The compound (D) is :

  (a) PbSO<sub>4</sub> □ (b) ZnSO<sub>4</sub> □

  (c) MgSO<sub>4</sub> □ (d) BaSO<sub>4</sub> □
- - (c)  $CaCrO_4$   $\Box$  (d) none of these  $\Box$ 1. The metal nitrate (A) is:
    - (a)  $Ba(NO_3)_2$   $\Box$  (b)  $Pb(NO_3)_2$   $\Box$  (c)  $Ca(NO_3)_2$   $\Box$  (d)  $KNO_3$   $\Box$

# Solution

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## Practice Paper: 5 ....

1. (a)

Let xL of A and yL of B be mixed to form 2L of 0.2 N HNO<sub>3</sub> solution

$$x + y = 2$$
 ... (i)  
 $y \times 0.1 = 2 \times 0.2$  ... (ii)

 $x \times 0.5 + y \times 0.1 = 2 \times 0.2$ 

Solving both the equations, we get y = 1.5 L and x = 0.5 L

2. (b)

$$1 \text{ N KMnO}_4 = 10 \text{ mL } 1 \text{ N H}_2\text{O}_2$$

Mass of 
$$H_2O_2 = \frac{17 \times 10}{1000} = 0.17 \text{ g}$$

Mass of impure  $H_2O_2$  soln. =  $\frac{1000}{85} \times 0.17 = 0.2$  g

3. (d)

$$TII_3 \Longrightarrow TI^+ + I_3^-$$

4. (b)

5. (b)

Ni<sup>2+</sup>

$$[Ag(CN)_2]^- - sp$$
 hyb.  
 $[Co(CN)_6]^{3-} - d^2sp^3$  hyb.

6. (c)

 $XeF_4$  is symmetrical with square planar shape, so the resultant dipole moment is zero.



XeF<sub>4</sub>

KClO<sub>3</sub> is used in fireworks and safety matches.

8. (

In BF<sub>3</sub>, there is back bonding in between boron and fluorine which imparts double bond character.

As BF<sub>3</sub> forms an adduct, the back bonding disappears and hence, double bond character disappears and the bond length between boron and fluorine increases a bit.

9. (d)



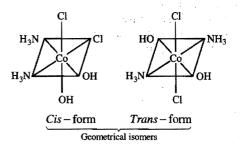
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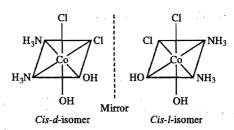
10. (a, b, c)

Oxides of phosphorus are dimeric in nature, P<sub>4</sub>O<sub>6</sub> and P<sub>2</sub>O<sub>10</sub>.

11. (a, c, d

[CoCl<sub>2</sub>(OH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Br and [CoClBr(OH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl are ionisation isomers.





12. (a, c)

The structure of  $CS_2$  is linear S=C=S, similarly the structures of  $HgCl_2$  and  $C_2H_2$  are linear, Cl-Hg-Cl,  $HC\equiv CH$ .  $SnCl_2$  and  $NO_2$  have angular structures.

13. (a, b, d)

14. (4)

H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (Pyrophosphoric acid) is formed when H<sub>3</sub>PO<sub>4</sub> is heated at 250-260°C.

$$2H_3PO_4 \xrightarrow{250-260^{\circ}C} H_4P_2O_7 + H_2O_7$$

This acid contains 4-OH groups i.e., 4 ionisable hydrogen atoms, thus it can form four series of salts.

15. (6)

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 6CO + 3(NH_4)_2SO_4$$

16. (2)

 $S_8$  molecule has the following structure. Each sulphur atom is in  $sp^3$  hybridized state.



Ratio = 16/8 = 2

Number of lone pairs = 16 Number of S—S bonds = 8 17. (2)

$$MnO_4^- + 5e \longrightarrow Mn^{2+}$$

Since 1 mole of  $MnO_4^-$  accepts 5 moles of electrons, therefore, 5 moles of electrons are lost by 1.67 moles of  $M^{x+}$ 

:. 1 mole of  $M^{x+}$  will lose electrons =  $\frac{5}{1.67}$  = 3 mol (approx.)

Since  $M^{x+}$  changes to  $MO_3^-$  by losing three electrons.

$$x = 5-3 = 2$$

18. (b) 19. (c)

20. (a)

21. (c)

Be has fully filled  $2s^2$ -orbital which gives a relatively more stable electronic configuration.

**22.** (a-r, s); (b-p, r); (c-p, r); (d-q, s)

23. (a-p, q); (b-p, s); (c-p, q, r); (d-p, r)

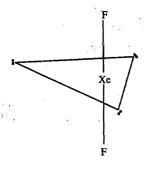
24. (a-q, r); (b-p); (c-p, s); (d-q)

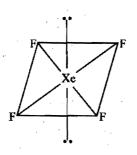
25. (b)



sp<sup>3</sup>d hybridization—See-saw shape

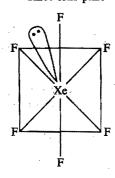
26. (a)

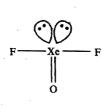




Three lone pairs

Two lone pairs





One lone pair

Two lone pairs

27. (b)

28. (d) 29. (b) 30. (a)

#### For Comprehension: 2

